PERFORMANCE OF MIXED CO_2/N_2 FOAM IN ENHANCED OIL RECOVERY FOR SANDSTONE RESERVOIRS

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

JANUARY 2017

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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Dedication

To my dear family, to my beloved country, and to the world.

ACKNOWLEDGMENTS

From the beginning till the end, praise be to Allah Almighty. He is who gave me knowledge. He is who gave me health. He is who gave me strength. And he is who gave me determination.

I would like to thank KFUPM for this precious opportunity to pursue further study after undergraduate level. The quality of the graduate program provided by KFUPM opened the door for a potential success in academia.

Thanks to my supervisor, Dr. Rahul Gajbhiye, for his great support and guidance during this work. Thanks are extended to my other committee member, Dr. Sidqi Abu Khamsin and Dr. Abdullah Sultan. They provided me with knowledge and instructions necessary to complete this research, and it is an honor to have their names written in my thesis front.

For all the technical support I received, I want to deliver my thanks to Petroleum Engineering Department' and Center of Petroleum lab coordinators Dr. Abdulrauf Adebayo, Mr. Wasef Nofal, Mr. Abdulrahim Muhammadain, Mr. Abdulsamad Iddrisu and Mr. Assad Barri.

To all my friends and family, thank you for your unlimited support. This work is my gift to you.

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LIST OF ABBREVIATIONS

AOS	Alpha-Olefin-Sulfonate
EOR	Enhanced Oil Recovery
FS	Fluorosurfactant
GOR	Gas-Oil Ratio
MMP	Minimum Miscibility Pressure
MRF	Mobility Reduction Factor
OIIP	Oil Initially in Place
OOIP	Oil Originally in Place
RF	Recovery Factor
SAG	Surfactant-Alternating-Gas
So_i	Initial Oil Saturation
Sw_i	Initial Water Saturation
WAG	Water-Alternating-Gas
WOR	Water-Oil-Ratio

ABSTRACT

Full Name : Mohamed Hassan Awadh Adam

Thesis Title : Performance of Mixed CO_2/N_2 Foam in Enhanced Oil Recovery for Sandstone Reservoirs

Major Field : Petroleum Engineering

Date of Degree : January 2017

Carbon dioxide flooding is an important enhanced oil recovery method. One major drawback of this technique is the early gas breakthrough due to unfavorable mobility ratio. One way to improve CO_2 injection in EOR is foaming the gas. Foam is generated when gas and surfactant are mixed together in the reservoir. The flooding of foam considerably reduces the gas mobility, which allows the gas to cover more regions in the targeted reservoir, which wouldn't be touched due to variations in permeability, and mobilize the left-behind oil. Thus, oil recovery by gas is enhanced. However, at typical reservoir conditions CO_2 exists at supercritical conditions. The ability of CO_2 to create foam is reduced.

A previous study (Siddiqui et. al 2016) conducted a set of experiments to optimize the performance of CO_2/N_2 foam at supercritical conditions in sandstone cores. Their optimized formula of foam injection (injection rate, foam quality and N_2 fraction) proved to generate a stable foam. Starting from their findings, this work tested the performance of CO_2/N_2 foam in oil-saturated sandstone cores.

Several coreflooding tests were conducted to assess the oil recovery by foamed CO_2 or foamed CO_2/N_2 mixture in sandstone cores. Two types of surfactant were used:

fluorosurfactant (FS-51) and alpha-olefin-sulfonate (AOS). N-decane was used as a model oil in all these experiments, with the test temperature maintained at 50°C. Every gas or foam flooding was preceded by brine flooding to simulate the behavior in the industry.

The experimental work indicated an improved performance of foamed gas over pure gas injection. The oil recovery by foam was better than by gas injection. Also, CO_2 foam performance was better than CO_2/N_2 mixture foams. Additionally, fluorosurfactant showed its ability to generate foam in high-saline environment.

ملخص الرسالة

الاسم الكامل: محمد حسن عوض ادم

عنوان الرسالة: أداء رغوة خليط ثاني أكسيد الكربون والنتروجين في تحسين استخلاص النفط من الصخور الرملية.

التخصص: هندسة البترول

تاريخ الدرجة العلمية: يناير 2017

يعتبر استخدام غاز ثاني اكسيد الكربون من الطرق المهمة لتحسين استخلاص النفط. إحدى أهم سلبيات هذه الطريقة هي الاختراق المبكر للغاز بسبب النسبية السلبية للحركة. من الحلول للتغلب على هذه السلبية هي تكوين الرغوة. تتكون الرغوة عندما يتم ضخ الغاز وخافض التوتر السطحي (surfactant) معاً إلى داخل المكمن. ضخ الرغوة داخل المكمن يساعد في تقليل حركة الغاز مما يؤدي إلى وصول الغاز إلى مناطق جديدة لم يتم الوصول إليها قبلاً وتحريك النفط. لكن عند ظروف المكمن يتواجد غاز ثاني أكسيد الكربون في حالته الحرجة مما يجد صعوبة في تكوين الرغوة.

في دراسة سابقة أجريت العديد من التجارب للحصول على الأداء الأمثل لرغوة خليط ثاني أكسيد الكربون والنتروجين في الصخر الرملي عند الظروف الحرجة. العوامل المثالية (معدل الضخ، جودة الرغوة ونسبة النتروجين) ضمنت الحصول على تكوين رغوة مستقرة. ابتداءاً من نتائج هذه الدراسة، هذا البحث يهدف إلى اختبار رغوة ثاني أكسيد الكربون والنتروجين في الصخور الرملية المحتوية على نفط.

تم إجراء العديد من اختبارات غمر العينات الصخرية لتقييم استخلاص النفط بواسطة رغوة ثاني أكسيد الكربون أو رغوة خليط ثاني أكسيد الكربون والنتروجين في الصخور الرملية. تم استخدام نوعان من خوافض التوتر السطحي (AOS) و (Fluorosurfactant). سائل (n-decane) تم استخدامه كمحاكاة للنفط في كل التجارب تحت درجة حرارة 50 درجة مئوية. كل عملية ضخ للغاز أو الرغوة سبقها صخ الماء المالح ليحاكي تسلسل العمليات في الحقول النفطية.

نتائج التجارب أظهرت تحسن استخلاص النفط عند استخدام الرغوة مما كان عليه باستخدام الغاز فقط. كما أظهرت التجارب أن استخدام رغوة ثاني أكسيد الكربون يعطي نتائج أفضل من استخدام رغوة خليط ثاني أكسيد الكربون

والنتروجين. بالإضافة إلى ذلك فإن خافض التوتر السطحي (Fluorosurfactant) كان جيداً في تكوين رغوة في الظروف شديدة الملوحة.

CHAPTER 1

INTRODUCTION

Oil and gas are the main sources of energy around the world and the demand for them has never slowed down. However, most of petroleum reservoirs nowadays are mature and the production from these reservoirs by natural drive or secondary drive, water flooding or immiscible gas flooding, is declining. Since decades, oil companies focused their efforts to explore and develop techniques that are more advanced to extract oil that could not be recovered by primary and secondary methods and, hence, boost the oil production. These methods are called Enhanced Oil Recovery (EOR) methods.

EOR techniques are implemented in the field whenever the production from primary or secondary recovery phase does not seem to be economically feasible. In general, primary and secondary recovery mechanisms produce between 20-50% of the oil originally-in-place (OOIP), depending on oil and reservoir properties [1]. EOR methods are classified into three broad categories: thermal methods, chemical methods and gas injection. In thermal methods, heated fluids are injected into reservoirs usually containing highly viscous oil to mobilize it. In chemical methods, various chemicals are injected to increase oil mobility. In gas injection, gases like carbon dioxide, hydrocarbon gases or nitrogen are injected to improve the oil displacement. Gas injection account for about sixty percent of EOR production in the United States, thermal flooding accounts for nearly forty percent and chemical methods contribute with nearly one percent [2].

CO_2-EOR is one of the efficient methods in recovering oil from depleted reservoirs. It has several attractive features that favor its application among other EOR methods. Carbon dioxide is a proven solvent for mobilizing and recovering residual oil left behind after conducting reservoir waterflood. Under certain conditions of pressure, temperature and oil composition, carbon dioxide can achieve miscibility with oil which eventually helps in decreasing oil viscosity, and causing the oil to swell and lower the interfacial tension. Also, carbon dioxide can be found in large quantities either from the natural resources or as a byproduct form many industrial facilities. Thirdly, with the increasing concern with green-house gas emission and its role in causing the global warming, many attempts were made to capture carbon dioxide and store it underground by implementing it in EOR projects.

Despite all the attractive features of CO_2-EOR, it has some challenges that limit its success in many cases. CO_2 is more mobile than the oil in the porous media because it is less viscous. This condition of unfavorable mobility leads to viscous fingering which results in early gas breakthrough in the producing wells. Ultimately, a large portion of the field is partially swept by the injected CO_2 and considerable quantities of oil is left behind, which is a result of poor volumetric sweep efficiency. If the reservoir contains some degree of heterogeneity, this problem can be more severe. Furthermore, the big contrast in densities between CO_2 and oil leads to CO_2 overriding the liquid phase present in the reservoir.

Foam is one of the methods proposed to reduce the mobility of the injected gas. Gas breaks into bubbles separated and stabilized by the surfactant. The occurrence of foam causes a drastic reduction in gas mobility which is essential for improving the volumetric sweep efficiency during immiscible or miscible gas flooding of oil reservoirs. For foam to be generated in the porous media, gas and surfactant are injected simultaneously or

alternatively at specific conditions. Foam has other applications in the petroleum industry, beside EOR mobility control agent, such as acid diversion, gas-shutoff, and water-shutoff [3].

The main objective of this study is to examine the performance of oil displacement by a novel foam system in which the gaseous phase consists of a mixture of CO_2 and N_2. Foam flooding experiments are conducted at conditions above the supercritical conditions of CO_2. At supercritical conditions, CO_2 becomes denser and tends to generate weak foam. Nitrogen is added to carbon dioxide to examine its effectiveness in improving the CO_2 ability to generate strong foam at supercritical conditions. The performance of CO_2/N_2 foam is compared to CO_2 foam in terms of displacement efficiency to see whether CO_2/N_2 foam is better than CO_2 foam at supercritical conditions. In addition, the CO_2/N_2 ratio, type of surfactant, foam quality and injection rate are varied in each experiment to study their effects on CO_2/N_2 foam flooding performance.

Thesis organization

Chapter 2 reviews the literature in topics that involve the use of carbon dioxide in EOR, the introduction of foam into EOR and the behavior of foam from the perspective of lab tests and fields applications. Chapter 3 presents the objectives behind conducting this research and identify the challenges of using foam in EOR. Chapter 4 explains, in detail, the methodology, the equipment and materials, and the work strategy to conduct this research. Chapter 5 illustrates all the results of the experiments accompanied by a thorough analysis and discussion. Chapter 6 presents the conclusions and recommendations for the future research in this area of study.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide EOR

The use of carbon dioxide in enhanced oil recovery was firstly patented in 1952. Since then, CO_2-EOR proves its effectiveness in producing oil that could not be recovered through primary or secondary methods. By 2010, the number of CO_2-EOR projects around the world had reached 127, from which 112 projects were in the United States [4]. Today, two major actions are pushing for further development of CO_2-EOR. Firstly, experts from the environmental, industrial and scientific fields are aware of the dangers of anthropogenic emissions of greenhouse gases, including carbon dioxide, methane and nitrous oxide, into the atmosphere, and efforts are made to avoid, or at least, lessen the effects of global warming. Secondly, the increasing number of population demands that more sources of energy to be secured and exploited [5]. Utilizing CO_2 in enhancing the oil recovery from petroleum reservoirs proves to be a reliable and efficient technique to fulfill the two above-mentioned goals.

2.2 Advantages of CO_2 in EOR

CO_2 flooding as an EOR technique is preferential over other gases for the following reasons. Miscibility between CO_2 and reservoir oil is achieved at lower pressure than with hydrocarbon gas. CO_2 flooding has relatively minimum problem of gas overriding due to its high density at typical reservoir conditions. It aids recovery by solution drive and is useful over a wider range of crude oil types than hydrocarbon gas flooding [6,7]. The

critical pressure of CO_2 is 7.39 MPa, or 1073 psia, and the critical temperature is 87.8 °F, or 31°C. At typical reservoir conditions, CO_2 is present as dense or supercritical fluid. If CO_2 is injected into reservoir with pressure above its critical pressure, CO_2 density becomes very high; sometimes it approaches the density of reservoir crude oil. In other words, CO_2 can adopt properties midway between a gas and a liquid with a density like liquid and a viscosity like gas. At these conditions, CO_2 characteristics of density and viscosity are relatively high, which make the displacement front more stable by naturally mitigating gravity segregation and viscous fingering to some degree during gas injection EOR [8].

2.3 Characteristics of CO_2-EOR

Reservoir conditions, reservoir fluids properties and CO_2 purity determine whether CO_2 is injected at miscible or immiscible state. Miscible or near miscible displacement between oil and CO_2 works by the extraction of hydrocarbons from the oil into the CO_2 and by the dissolving of CO_2 into the oil. At pressure above the minimum miscibility pressure (MMP), interphase mass transfer can occur to such a degree that interfaces between the oil-rich and CO_2-rich phases disappear and miscibility or partial miscibility results. Sometimes it is not possible to achieve miscibility between injected CO_2 and reservoir oil, e.g. high value of the minimum miscibility pressure (MMP). Immiscible displacement occurs at pressure less than MMP, where less interchange of components and mass transfer between injected CO_2 and reservoir fluid takes place. Generally, the recovery achieved with miscible displacement is much higher than immiscible displacement. Immiscible CO_2 flooding is best suitable for reservoirs that contain moderately viscous oils of density less than 25 °API, where miscible or near miscible flooding is suitable for light-to-medium oils [1,2].

Fatemeh et al. performed an experimental study to assess the performance of CO_2 flooding and storage into sandstone cores saturated with oil. Three experiments were run at different miscibility conditions: immiscible, near-miscible and miscible. Their observations showed that at miscible and near-miscible flooding, the oil recovery was nearly the same, 73% of OIIP, but was less by 18% in immiscible flooding. The highest CO_2 storage efficiency was achieved in near-miscible flooding [3].

If the injected CO_2 is not pure and contains some impurities, the minimum miscibility pressure is increased and gets higher as the impurity content rises [1]. Zhang et al. investigated the effect of CO_2 impurities on gas injection EOR based on coreflood experiments. When carbon dioxide was contaminated with nitrogen, methane or any mixture of them, the measured MMP was unfavourably higher compared to MMP of pure CO_2 gas. CO_2 gases contaminated with H_2S or SO_2 showed lower MMP. In addition, they showed that mixing CO_2 gas with propane will lower its MMP [4].

2.4 Limitations of CO_2-EOR

As EOR flooding with carbon dioxide proves to be advantageous in many cases, however, it has several disadvantages that limit its success. The volumetric sweep efficiency of CO_2 flooding is poor due to unfavorable mobility ratio of CO_2 compared to reservoir oils. Because CO_2 viscosity is extremely lower than reservoir oil, CO_2 is more mobile than the oil which causes the viscous fingering, and eventually, an early breakthrough. The early gas breakthrough means that most of the injected gas is circulated through the reservoir without contacting or displacing oil. Viscous fingering also acts to destroy the zone of dynamic miscibility, which was achieved by extraction into the CO_2, of intermediate hydrocarbon components in the oil. In addition, gravity override takes place due to the

large contrast in density between CO_2 and reservoir oil, and the high vertical permeability. In a heterogeneous formation, these issues worsen [5].

To tackle these shortcomings and improve the displacement efficiency of CO_2 flooding, several attempts and solutions were proposed and tried. Water-alternating-gas (WAG) is one of the proposed solutions because it combines the improved displacement efficiency of the gas flooding with an improved macroscopic sweep by the injection of water. This has resulted in reducing the gas mobility which improved the recovery [6]. Despite its success in some field operations, it is not an ideal method. The fronts formed around the injection well after injected water is followed by CO_2, are unstable. CO_2 will tend to finger through the high-water saturation zones and may bypass regions where oil saturation is still high. In addition, the dynamically developed miscibility zones are destroyed by the water injection. Other solutions proposed to improve the sweep efficiency involve the use of chemical gels. Addition of foaming solutions combined with CO_2 injection generates foams which stand as an efficient solution for CO_2 flooding mobility control.

2.5 Foam in EOR

The introduction of foam injection into EOR was reported by a work conducted by Bond and Holbrook, whose 1958 patent describes the use of foams in gas-drive processes. In their work, a water-soluble surface active agent with foam-producing characteristics was injected into an underground formation as an aqueous slug. Then injected gas was forced through the aqueous solution that produced a foam front between the injected gas and the reservoir fluids which greatly reduced the mobility of the gas phase and increased the displacing ability of the injected gas [7]. Later, Fried demonstrated the potential of foam to lower the mobility of an injected gas phase. Fried generated the foam in a cylinder by

dispersing fine air bubbles beneath the surface of a surfactant solution. This foam was flowed but only with much difficulty through a highly permeable matrix. A highly viscous foam was indicated, suggesting that, indeed, foam might control the mobility of gases during oil displacement [8].

Foam in porous media is mainly a mixture of gas and liquid where the gas phase is discretized into bubbles separated by thin films, called lamellae, and the continuous liquid phase is made of a surfactant solution that stabilizes the lamellae and wets the rock. The discontinuous gas bubbles are in the order of pore size in the rock and stretch across the gas-occupied pore spaces, whereas the wetting surfactant solution fills the smallest pore channels and coats the pore walls. It is the discontinuous nature of the gas which causes foam to exhibit low flow mobility in porous media. Clearly, if the lamellae keeping the gas disconnected continually rupture, the foam is destroyed and is no longer an effective mobility control agent [9].

The mechanisms by which foam helps in recovering additional oil can be summarized as follows. Firstly, foaming CO_2 drastically increases its viscosity which lowers its mobility and makes the displacement process more stabilized. Secondly, foam is created easily in high permeable areas. Thus, further gas, or foam, injected will be diverted into areas of low permeability or unswept zones where higher oil saturation is expected to reside. This will improve the areal and horizontal sweep efficiency. Thirdly, the presence of surfactant in foam will result in reduction the interfacial tension between the oil and rock. Fourthly, because the gas is in more contact with oil, the interfacial mass transfer between gas and oil plays an important role in mobilizing the oil droplets by dissolution, viscosity reduction and swelling [10]. If not succeeded at recovering additional oil, foam application, at least,

will delay the time at which the injected gas breakthroughs into the producing wells and reduce the amount of gas produced, which in turn cuts the gas handling costs.

2.6 Foam characterization

Physically, foams are characterized by two measures. 1) Foam quality is the volume of gas in a foam expressed as a percent or fraction of the total foam volume. In terms of flowrate, foam quality is the ratio between the gas flowrate, and the sum of the total flowrate. Foam quality can vary with both temperature and pressure because the gas volume can change, and gas dissolved in the liquid phase can come out of solution. Foam qualities can be quite high, approaching 97% in many cases. A foam with quality greater than 90% is a dry foam. 2) Foam texture is the average bubble size. There is a large range possible for the texture ranging from the colloidal size (0.01-0.1 μm) up to that of a macro-emulsion. If the average bubble size is much smaller than the pore diameter the foam flows as dispersed bubbles in the pore channels. If the average bubble size is larger than the pore diameter the foam flows as progression of films that separate individual gas bubbles. Considering typical foam textures and pore sizes, the latter condition is more nearly realized particularly for high-quality foams. Foam texture is a function of surfactant concentration, surfactant type, pore structure, pressure, and injection rates. In addition, foams with a large distribution range are more likely to be unstable [11].

2.7 Foam in porous media

Gas flow in porous media in the presence of foam should be considerably different from gas flow in the absence of foam [12]. Foam is porous media can occur at three situations, as Figure 1 illustrates.

1) Foam may not be generated initially, or the foam has been destroyed or destabilized because of the high capillary pressure environment, strongly oil-wet formation or existence of high oil saturation. This situation identically a conventional gas/liquid two-phase flow (Figure 1A).
2) Weak foam which exhibits moderate increase in effective foam viscosity that leads to a moderate increase in pressure gradient or reduction in water saturation (Figure 1B).
3) The presence of numerous foam films forms very fine-textured foams, which is referred to as strong foams. Once formed, strong foams may increase effective foam viscosity (or decrease relative gas mobility, equivalently) by up to several orders of magnitude, exhibiting a dramatic increase in pressure gradient or reduction in water saturation (Figure 1C) [13].

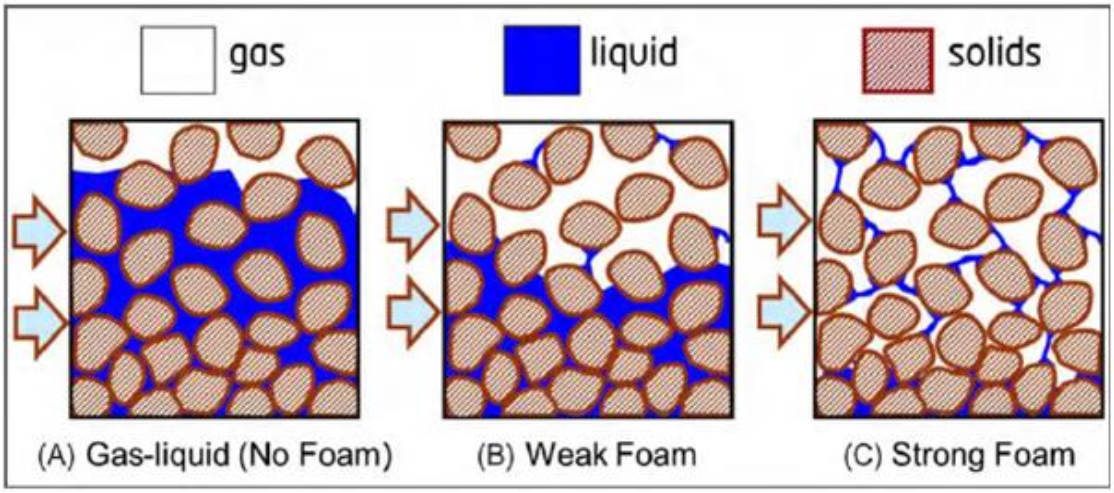

Figure 1: Schematic of gas-liquid flow, weak foam and strong foam in porous media.

2.8 Mobility reduction by foam

Foams flowing in permeable media can drastically reduce the mobility of a gas phase. Figure 2 shows the steady-state mobility of foams of differing quality in Berea cores at three different permeabilities. The mobility of the foam decreased with increasing quality until the film between the gas bubbles begins to break. At this point the foam collapses and the mobility increases to the gas mobility. Foams are effective in reducing the mobility at all three permeability levels but the effect of foam quality is relatively larger at the highest permeability. The mobility reduction caused by the foam can be viewed as an increase in the effective viscosity of a single-phase flow or as a decrease in the gas phase permeability. In the first case, the effective viscosity comes from dividing the measured mobility into the single-phase gas permeability. In the second case, the gas phase permeability follows from multiplying the measured mobility by the gas viscosity [11].

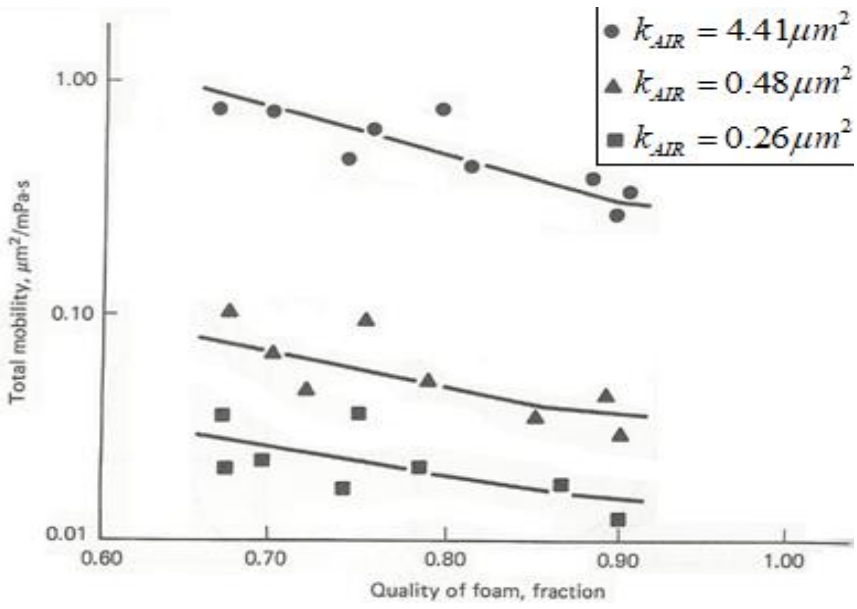

Figure 2: Effective permeability-viscosity ratio versus foam quality (Lake, 1989).

2.9 Foam generation and placement

The nature of problem dictates the technique by which foam is delivered to the zone of treatment. Foam is used mainly to fulfill three tasks. 1) Foam is used as blocking/diverting agent to achieve uniform distribution of gaseous injectant into treated zones and enhance the vertical sweep efficiency. 2) As in-depth mobility control agent, foam is used as a solution to unfavorable mobility during gas flooding. In these two tasks, foam is placed in the injectors. 3) In the third task, foam is placed in production wells to mitigate an override problems of gas coning, in gas miscible flooding, and steam override, in cyclic steam injection.

There are three approaches of foam generation. 1) Pre-formed foam is generated outside porous medium, either at the surface using a foam generator, through the tubing during downward flow or in the perforations. 2) Co-injection foam is formed in-situ during co-injection of surfactant solution and gas. 3) SAG foam, is generated by alternate injection of surfactant solution and gas [10].

2.10 Foam stability

Foam stability is an important factor that guarantee the success of foam-assisted EOR in field applications. Stable foam diverts injected gas into low-permeability zones that contains considerable amount of oil to improve the sweep efficiency and, in addition, reduces the mobility of injected gas to maintain a uniform displacement. Several factors can affect the stability of foam, e.g. type of surfactant, type of reservoir fluids, mode of placement, gas properties, reservoir characteristics.

Because the foam is a thermodynamically unstable system, its long-term stability during a field application is difficult to maintain. Foam stability can be considerably deteriorated by

the presence of residual oil. Oil saturation should be low enough to have minimal effect on foam strength. In addition, high reservoir temperature is another concern. Surfactants generally tend to degrade before they fulfill their long-term duty, and surfactant loss in a reservoir due to adsorption in porous media results in a large consumption of chemicals [14][15]. Furthermore, adsorption of the surfactant on the rock surface decreases the surfactant concentration and therefore shortens the distance that the surfactant will propagate into the oil reservoir before its concentration becomes too low to be effective in generating the foam Thus, the choice of surfactant is an important key in the success of a foam injection process. A suitable surfactant should be capable of generating ample and stable foam in the presence of reservoir rock and oil at high pressures and temperatures. The surfactant should have low adsorption on the rock. [16].

Kapetas et al. investigated the effect of temperature on foam stability and strength. The surfactant used was AOS and the temperature ranged between 20 and 80°C. Their findings revealed that the rise temperature destabilized the foam. When the temperature reached 80°C, the apparent viscosity of foam decreased by 50% [17]. Amro et al. investigated the effect of pressure on foam stability with CO_2 and N_2 foams in bulk foam experiments under pressures up to 10 MPa. They showed that CO_2 foam stability was decreasing as the pressure increased and explained this behavior as gas permeation between adjacent bubbles was strongly enhanced. In addition, CO_2 exerts an extraction effect on the surfactants; their concentration is reduced in the film phase leading to a decreasing viscoelasticity and hence destabilizing the foam film. In contrary, N_2 foam was not affected by the change in pressure [18].

Yin et al. studied the behavior of CO_2 foam when Berea sandstone core is initially saturated with oil before the start of foam flooding. In terms of differential pressure their results showed that as the oil saturation inside the core decreased, pressure drop across the core increased indicating the increased foam stability. Figure 3 illustrates the destabilizing effect of oil on foam as the oil saturation increased [19].

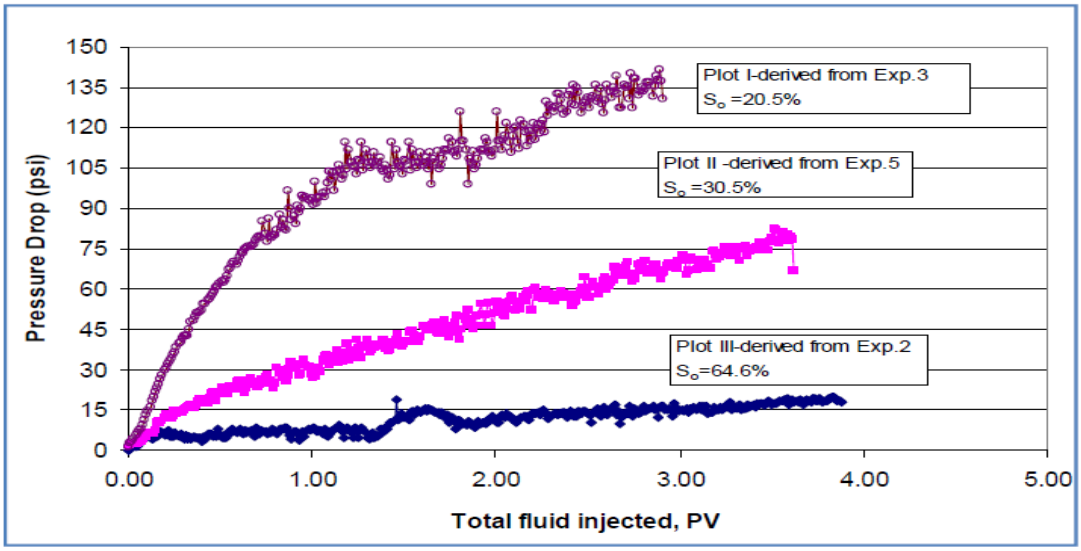

Figure 3: Effect of oil saturation on CO_2 foam flooding (Yin et al., 2009).

However, it is possible to generate foam with materials other than surfactants. In a study by Yu et al. nanoparticles were used instead of surfactants to generate stabilized foam. They argued that surfactant-stabilized foam lacks the ability to maintain its long-term stability and suffers from adsorption loss. Nano-silica dispersion with particle concentration in the range of 4000 to 6000 ppm was used to generate stable CO_2 foam in observation cells. Increased brine concentration in nanoparticle could inhibit CO_2 foam generating. Adding small amount of surfactant to the nano-silica dispersion was observed to improve the generation of foam [15].

2.11 Foam coreflood experiments

Solbakken et al. investigated the effect of CO_2 density on the performance of CO_2 foam. In their study, they generated the foam using AOS surfactant as the foaming agent and at foam quality of 80%. A set of coreflood experiments on Berea sandstone cores were conducted at different conditions, pressures from 30 to 280 bar and temperatures of 50 and 90°C. They showed that the CO_2 density varied from low, or gas-like, density to high, or liquid-like, density. Increasing the pressure resulted in increasing pure-CO_2 density, holding the temperature constant, whereas increasing the temperature resulted in decreasing pure-CO_2 density, holding the pressure constant. It was evident from their findings that increasing CO_2 density would reduce its ability to generate stronger foam. In terms of the Mobility Reduction Factor (MRF), an expression used to evaluate the magnitude of the gas mobility reduction caused by foam in laboratory foam tests, strong foam was characterized with high value of MRF when CO_2 density was lower [20].

Farajzadeh et al. made a comparative study of CO_2 foam and N_2 foam flooding in porous media initially saturated with surfactant at high and low pressures and temperatures. Flooding conditions of 1 bar and 20°C met the subcritical conditions of injected CO_2 and Flooding conditions of 90 bar and 50°C met the supercritical condition of CO_2. N_2 injected at both flooding conditions was subcritical. The surfactant used was alpha-olefin-sulfonate (AOS) and the porous medium used was consolidated Bentheimer sandstone. The experiments have clearly demonstrated that under a SAG scheme CO_2 foams are weaker than N_2 foams at both low and high pressures. Foaming of CO_2 builds up lower pressure drop over the core at both low and high pressures when compared to N_2. Gas solubility in surfactant was highly responsible for this behavior because CO_2 is about 55 times more

soluble in water than N_2. So, more volume of injected CO_2 than N_2 will be soluble in surfactant which reduce the volume available for foaming. In addition, the coalescence rate of CO_2 foam bubbles was higher than that of N_2 foam bubbles. Other factors contributed to this behavior beside solubility, but with less intensity, are interfacial tensions, pH effects, type of surfactant and the possible wettability effects [16].

Farajzadeh et al. conducted a set of experiments on supercritical CO_2 performance on oil recovery with different flooding strategies. For each experiment, sandstone cores were saturated with brine, then flushed by synthetic oil, brine was injected until no more oil is produced and then one or two pore volumes of AOS surfactant was injected. Afterwards, gas or foam injection would start. The different gas flooding strategies conducted on this study were CO_2 gas flooding, CO_2 foam flooding, and CO_2 gas flooding followed by CO_2 foam. Supercritical CO_2 injection was done at miscible and immiscible conditions. Results revealed that miscible flooding of CO_2 foam gave the highest oil recovery by 86% by recovering 40% additional oil. Immiscible CO_2 foam flooding recovered incremental oil by 21% to achieve total recovery of 65%. Immiscible CO_2 gas flooding followed by CO_2 foam recovered 19% additional oil to achieve total recovery of 84%. For CO_2 foam experiments it was observed that the pressure drop in the water-saturated part of the core was higher than in the part where oil was present because of the destabilizing effect of oil on foam [21].

Simjoo and Zitha conducted CT scanning on sandstone cores flooded with immiscible foam and made a comparison with nitrogen flooding, after the core was water-flooded. They used three different surfactant concentrations, 0.1, 0.5 & 1 wt%, and nitrogen as the gaseous phase. In terms of incremental oil, foam displacement performance was better than

gas flooding. After 3 PV of injection, nitrogen, 0.1 wt% foam, 0.5 wt% foam and 1 wt% foam flooding recoveries were 4, 5, 12 and 16 respectively. For longer injection time, 1 wt% foam recovered 29% of additional oil were 0.1 and 0.5 wt% foams recovered 13 and 28% of OIIP respectively. It was also observed that the time of foam breakthrough to occur is delayed with increasing the surfactant concentration. In terms of foam mobility reduction factor (MRF), increasing the surfactant concentration gave larger MRF which indicated better sweep efficiency and more stable foam in presence of oil [22].

2.12 Foam in field applications

The first field application of foam as a mobility-control agent started in the Siggins field in Illinois, United Stated, in 1964. Air was used as the gas phase and the foaming agent was a modified-ammonium-lauryl-sulfate surfactant, named as O.K. Liquid. Before the start of foam project, the water-oil ratio (WOR) reached a value of 25:1, after a waterflooding project. Execution of the foam project resulted in uniform distribution of the surfactant into the layers and large reduction in WOR to reach 12:1. Mobilities of both air and surfactant were observed to be reduced by 50 and 35% respectively.

Between 1990 and 1991, the North Ward-Estes field in Texas witnessed the most successful foam application. The formation consisted of fine-grained sandstones to siltstones and was very heterogeneous. The field which was operated by Chevron started oil production by primary drive in 1929, and started to be water flooded in 1955. When CO_2 flooding started in 1989, the remaining oil estimated to be around 77 million barrels, 54% of OIIP. However, the problem of poor sweep efficiency arose and led to an early gas breakthrough. Eventually, foamed CO_2 flooding was proposed as a potential solution. The surfactant used was Chaser CD-1040, an alpha-olefin sulfonate (AOS), because it had good

selective mobility reduction and residual mobility reduction factors. Two modes of placement were evaluated, SAG injection and co-injection. The quality of foam was in the range of 50-80%. For the offending well, the GOR decreased 9-folds, while oil production increased 15 times and water cut decreased. The foam successfully diverted CO_2 from the thief zone to unswept regions. The utilization of CO_2 was enhanced considerably [13,23].

Another successful application of foam-assisted EOR occurred in the East Vaccum Grayburg San Andres Unit, New Mexico, which was operated by Philips Petroleum Company. Several wells suffered from an early breakthrough of CO_2 and resultant volumetric sweep efficiency after WAG operation was poor due to a permeability contrast. SAG cycles were implemented in this pilot test. For a duration of four years, the injection pressure increased by 25%, 12% of the total injected fluid successfully diverted from the thief zone to the other zones, the gas/oil ration declined by two-fold, and the oil production rate increased by two-fold. Three more wells produced oil in the pattern, which resulted in an oil rate increase by 10 to 20 times [13,23].

Ocampo et al. reported the application of foam injection in a pilot test in Cusiana field in Colombia, South America. Earlier coreflood experiments showed positive results obtained with foam flooding where it recovered between 10 and 17% additional oil. The field trial of foam flooding resulted in increasing the oil rate coupled with decreased GOR after two to three months after foam injection started. The functions of foam as gas-blocking and sweep-enhancer was effective to achieve these results [24].

CHAPTER 3

PROBLEM STATEMENT AND RESEARCH OBJECTIVE

From all EOR methods, CO_2 miscible flooding is the second most used and implemented technique, and the first method to be used in recovering light-to-medium oils. However, the major limitation with CO_2-EOR is the poor volumetric sweep efficiency due to unfavorable mobility ratio of CO_2 in compared to oil, which causes the early breakthrough of CO_2 that leaves considerable parts of formation untreated. To tackle this problem, foaming CO_2 was sought as a solution to reduce CO_2 mobility and achieve a piston-like displacement of oil. Eventually, the volumetric sweep efficiency could be improved and gas breakthrough could be delayed.

Usually, CO_2 are injected in deep reservoirs which meets the supercritical conditions of injected CO_2. Hence, it is essential to control the mobility of CO_2 flooding and stabilize the displacement of oil by foams. From the literature review it was seen that CO_2 at supercritical conditions generate unstable and weak foam. Supercritical CO_2 adopt properties midway between a gas and a liquid. More specifically, it behaves as a supercritical fluid above its critical temperature (304.25 K or 31.1°C) and critical pressure (7.39 MPa or 1071.8 psi), expanding to fill its container like a gas but with a density like that of a liquid. A strong and stable foam is essential in making a successful CO_2 flooding because strong foam stabilizes the displacement of gaseous injectant and diverts upcoming gas into low permeability zones. At the worst scenario, foamed CO_2 can delay the

breakthrough of CO_2 and minimize the GOR at producers, which cuts the gas handling costs.

Very limited studies in the literature involve investigating the foamed CO_2/N_2 mixture in EOR, as far as the author knows, except a study by Holm and Garrison [20] where immiscible CO_2/N_2 foam was injected in a field project. The current study is investigating the performance of foams generated by carbon dioxide mixed with nitrogen to improve its behavior at supercritical conditions. Nitrogen is added to carbon dioxide in different fractions and co-injected into sandstone cores containing residual oil. Two baseline experiments are conducted for comparison reasons, CO_2 flooding and N_2 flooding, to justify the use of foam as a mean for improving the displacement. The recovery of oil is compared between foamed CO_2 flooding and foamed CO_2/N_2 mixture flooding. Parameters that are changed will be foam quality, CO_2/N_2 ratio, injection rate and type of surfactant.

CHAPTER 4

METHODOLOGY

4.1 Materials

4.1.1 Salts

Mineral salts were used to prepare synthetic brine solutions, both formation brine and seawater brine. For that purpose, a group of mineral salts were used:

- Sodium chloride (NaCl)
- Calcium chloride ($CaCl_2$)
- Magnesium chloride ($MgCl_2$)
- Sodium sulfate (Na_2SO_4)
- Sodium bicarbonate ($NaHCO_3$)

4.1.2 Core samples

Berea sandstone cores were used to perform the coreflooding tests. All core samples were 12 inch in length and 1.5 inch in diameter.

4.1.3 Gases

Carbon dioxide (CO_2) and nitrogen (N_2) gases were supplied from Saudi Industrial Gas Company. CO_2 was used as an injection fluid and N_2 was used as injection fluid as well as to operate the valves in the coreflooding system.

4.1.4 N-decane

It is an aliphatic hydrocarbon. Less dense than water and insoluble in water. Several samples of this hydrocarbon were purchased from SIGMA-ALDRICH and MERCK, with 99+% purity.

It has a molecular weight of 142.28 and a density of 0.73 g/ml (or 62° API equivalently) at 25°C. In terms of density and weight, the n-decane resembles the light crude oils.

4.1.5 Surfactants

FS-51 is an amphoteric amine oxide-based fluorosurfactant that significantly reduces the surface tension of aqueous solutions and is also useful in providing sustained foam.

AOS is a type of anionic surfactant processed by α-olefin gas-phase sulfonation and continuous neutralization. It is good in making rich and fine foam.

4.2 Experimental apparatus

4.2.1 Coreflooding system

The coreflooding setup consists mainly of four parts: the fluid-delivery unit, the core unit, the production unit, and the data-acquisition and control unit. An illustration of this setup is shown in Figure 4.

The fluid-delivery unit, or injection unit, is made up of: 1) six floating-piston vessels, 2) five pumps, 3) stainless-steel flow lines, and 4) valves. The floating-piston vessels contain the injection fluids: n-decane, seawater brine, carbon dioxide, nitrogen, and surfactant solutions. Delivery pumps include four positive-displacement Quizix pumps, which are

controlled by the computer, and an ISCO Dual Syringe pump. Quizix pumps are installed inside the coreflooding system, whereas the ISCO pump is external.

The core unit includes a Hassler-type core holder and a foam generator. The Hassler-type core holder has a rubber sleeve within it and designed to accommodate the 1.5″ diameter and 12″ length core samples. Spacers are installed inside the core holder to fill the voids and adjust for shorter, or longer cores. The core holder is also provided with two ports to allow for applying the overburden pressure by filling the annulus between the sleeve and the core holder's body with water. An ISCO 100D syringe pump is used to apply and maintain the desired overburden pressure. The foam generator is 7-micron filter, which put upstream the core holder in foam flooding experiments.

The production unit is mainly the back-pressure regulator, which is located downstream of the core holder. Nitrogen is the medium used to impose the required back pressure. The back-pressure regulator is a normally-closed valve that obstruct the flow. When the outlet pressure from the core exceeds the back pressure, flow of fluids is allowed into the separator.

The data-acquisition and control unit consists of a desktop computer, pressure transducers, a data-acquisition box and software packages. This unit records real-time data when experiments are running to be displayed on the computer screen. The software packages also control the air-operated valves and the Quizix pumps.

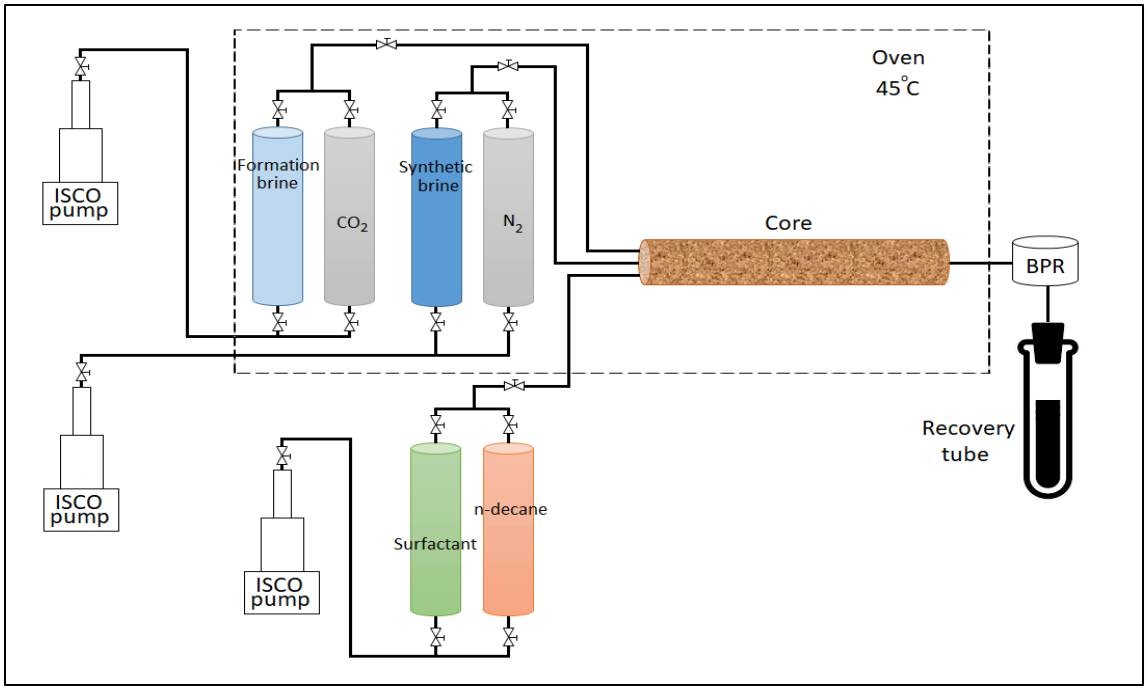

Figure 4: Schematic of the coreflood setup.

4.2.2 Laboratory balances

Two types of balances were used in this work. A digital analytical balance (Sartorius Cubis® Precision Balance MSE5203S-000-DE) was used to measure the weight of salts in making the brine solutions. The weighing capacity of this balance is 5200 g and its readability is 0.001 g. The other balance, a precision balance (Denver Instrument TR-4102 Toploading Balance), was used to measure both the dry and wet weights of the core. The weighing capacity of this balance is 4100 g and its readability is 0.01 g.

4.2.3 External pumps

Eldex Model BBB High Pressure Liquid Metering Pump. It has a flowrate range of 1-100 cc/min and high pressure capabilities up to 5000 psi. Also, Eldex Model AA High Pressure Liquid Metering Pump with a flowrate range of 0.2-10 cc/min and high pressure

capabilities up to 5000 psi. These two pumps were used in several tasks: to saturate the core initially with the synthetic formation brine, to clean the flow lines with toluene and distilled water, and to fill the coreflood system accumulators with injection liquids (seawater brine and surfactant solution).

Welch DirecTorr Model 8834 Vacuum Pump: it was used in many purposes; to empty nitrogen and carbon dioxide accumulators from air molecules before filling, to relief the high overburden pressure present around the core holder to release the core, and in the process of brine filtration.

ISCO 100DX Dual Syringe Pump: its flowrate ranges between 0.01 µl/min - 50 ml/min and pressure capability up to 10,000 psi. This pump was used to inject n-decane, nitrogen and surfactant solution, at different stages throughout the coreflooding.

4.3 Core flooding experiment procedures

4.3.1 Brine preparation

Each of the above-mentioned salts was added, in a specific amount, to distilled/deionized water. The amounts of salts added to prepare both the formation brine and seawater brine are shown in table1. Each salt was mixed with water separately to ensure it was dissolved completely and to avoid precipitation if salts were mixed together; a chemical reaction could take place. Then each salt solution was added to a bigger flask and water was added to obtain the required final volume. The final solution was stirred for a minimum of two

hours and then filtered using a filter paper. The resulting salinity of the formation brine and seawater are 253.88 and 67.708 TDS (total dissolved salts), respectively.

Table 1: Salts composition of brines.

Salts	Formation brine (g/liter)	Seawater (g/liter)
NaCl	157.18	41.17
$CaCl_2.2H_2O$	85.62	2.39
$MgCl_2.6H_2O$	10.60	17.64
Na_2SO_4	0.37	6.34
$NaHCO_3$	0.11	0.17
Total dissolved salts (TDS)	253.88	67.71

4.3.2 Core drying

The core was placed in an oven to be heated at a temperature of 45°C for 4 hours. This step is necessary to remove any moisture that might be trapped inside. After the heating, the dry weight of the core sample was measured. In later stage, when the core became saturated with brine, its wet weight was measured and used, along with the core dry weight, to estimate its porosity and pore volume.

4.3.3 Core saturation

The core sample was put in a high-pressure cell to saturate the core initially with the formation brine. The core was first evacuated from any trapped air, using the vacuum pump, for nearly 7 hours. Then, formation brine was pumped into the cell until the core became completely immersed. The pump kept injecting the brine until the pressure reached nearly 2000 psi. Then, the pump was stopped and the cell was closed and left overnight to let the formation brine penetrate the pores. Accordingly, the cell pressure would drop slightly. After the saturation, the core's wet weight was measured to calculate its porosity and pore volume.

4.3.4 Core placement and pre-start

The core was then placed inside the core holder. Before inserting the core holder inside the coreflooding system, a leakage test was done. An overburden pressure of about 800 psi was applied to check if there was any leak from the rubber sleeve. If leak was detected, the core would be removed from the core holder to replace the rubber sleeve. If not, after 4-6 hours, the core holder would be placed inside the system and the flow lines would be connected.

4.3.5 Formation brine flooding and oil injection

Several pore volumes of formation brine were injected into the core to fully saturate the core and build the pressure up to desired conditions. Injecting the brine was done with three flow rates, 0.5, 1 and 2 cc/min. At each flow rate the brine injection continued until the pressure drop across the core was stabilized. Afterward, the drainage process was started by injecting 1-2 PV of decane (the oil phase) at a rate of 0.5 cc/min, to displace the

formation brine and establish the irreducible water saturation. Injection continued until no more brine was produced. The amount of produced brine in the separator would represent the amount of oil trapped into the core. In this process, the initial oil saturation (S_{oi}), oil initially in place (OIIP), and the initial water saturation (S_{wi}) are calculated as follows:

OIIP = Volume of produced brine (cc)

$$S_{w_i} = \frac{\text{Pore Volume (cc)-Volume of produced brine (cc)}}{\text{Pore Volume (cc)}}$$

$$S_{o_i} = \frac{\text{Volume of produced brine (cc)}}{\text{Pore Volume (cc)}} = 1 - S_{w_i}$$

Then, the core was left for aging at 50°C for a duration of 3 days. The aim is to obtain a mixed wettability state.

4.3.6 The work plan

The table below shows all the experiments intended to be implemented during this research. The first two experiments are considered as baseline to assess the usefulness of using foam form the beginning.

Table 2: List of coreflooding experiments.

#	Scheme of flooding	Surfactant	Foam quality (%)	Injection rate (cc/min)	N_2 fraction (%)
1	CO_2	No surfactant	No foam	1	-
2	N_2	No surfactant	No foam	1	100
3	CO_2 foam	FS-51	80	1	0
4	CO_2/N_2 foam		80	1	20
5	CO_2/N_2 foam		90	1	20
6	CO_2 foam	AOS	80	1	0
7	CO_2/N_2 foam		80	1	20
8	CO_2/N_2 foam		90	1	20

CHAPTER 5

RESULTS AND DISCUSSION

This chapter illustrates, discusses and analyzes the results of eight coreflooding experiments conducted in this study. Each coreflooding experiment consisted primarily of four injection stages: formation brine injection, n-decane injection, waterflooding, and gas or foam flooding. During each fluid injection, a pressure drop across the core occurred due to flow resistance. The magnitude of this pressure drop varied according to the type of fluid injected and injection rate. These pressure drops were monitored and recorded during each experiment, and are presented in this chapter. Additionally, the oil recovery performances during waterflooding, gas flooding and foam flooding are analyzed and discussed for every experiment.

5.1 Cores properties

Prior to the start of coreflooding, the core sample was dried and saturated initially in a cell with formation brine to determine its pore volume and porosity, considering the brine density. Then the core was placed into the core holder and several pore volumes of formation brine were injected into the core.

The formation brine was injected at three different rates and a stabilized pressure drop across the core was measured for the individual injection rate. The obtained values of injection rate and corresponding stabilized pressure drop were used to calculate the absolute core permeability using the Darcy law. In the appendix, the graphs for pressure drop versus injection rate are shown for each experiment.

Afterwards, the n-decane was injected at a rate of 0.5 cc/min to displace the formation brine and establish the irreducible water saturation. The following table shows the main core properties for each experiment.

Table 3: Summary of core properties.

Experiment	1	2	3	4	5	6	7	8
Pore volume (cc)	71.30	54.15	65.35	71.45	63.04	64.03	83.38	83.38
Porosity (%)	20.5	15.6	18.8	20.6	18.1	18.8	24.0	23.0
Permeability (mD)	97.54	60.04	34.62	76.64	86.71	46.24	267.7	274.2
Initial water saturation (%)	25.0	33.5	34.2	34.2	33.4	40.0	47.0	38.0

5.2 Waterflooding

The oil recovery process started with waterflooding. The following stage would be either a gas flooding or foam flooding. Waterflooding conducted at a back pressure of 1700 psi and an injection rate of 1 cc/min. Between 3-4 PVs of seawater were injected until no more oil (n-decane) was recovered. Oil recovery was monitored and determined as a percentage of the oil-initially-in-place (OIIP).

5.2.1 Recovery performance

At the start of the waterflooding, the core is saturated with the movable oil (n-decane) and connate water (formation brine). The initial water saturation in all experiments ranged from 0.25-0.47. Figures 5 to 12 shows the oil recovery with the time-dependent injected pore volume. Generally, oil started to show up in the recovery tubes shortly before injecting 0.25 PV of water. Then the oil was being produced steadily with a considerable amount for a short time of water injection (0.25-0.5 PV of injected water). Finally, the oil recovery became nearly stabilized after the injection of 1 PV of water until the end of waterflooding when no more oil was produced anymore, only water was coming out of the core. The oil recovery factors achieved by the waterflooding ranged between 0.1 and 0.4. It indicates that the remaining oil inside the core, which was left behind after the water breakthrough, became immobile, and more of the water injection would not be able to recover additional oil.

It is worth noting that the increase in injection rate from 1 to 2 cc/min and from 2 to 4 cc/min did not change the rate at which oil was being produced (experiments 1, 3, 4 and 5). The following Figures 4-10 shows the oil recovery performance during the waterflooding for all the experiments. The remaining oil saturation ranged between 0.3-0.6. Figure 13 summarizes the recovery factors and the remaining oil saturation after the end of waterflooding stage for all eight experiments.

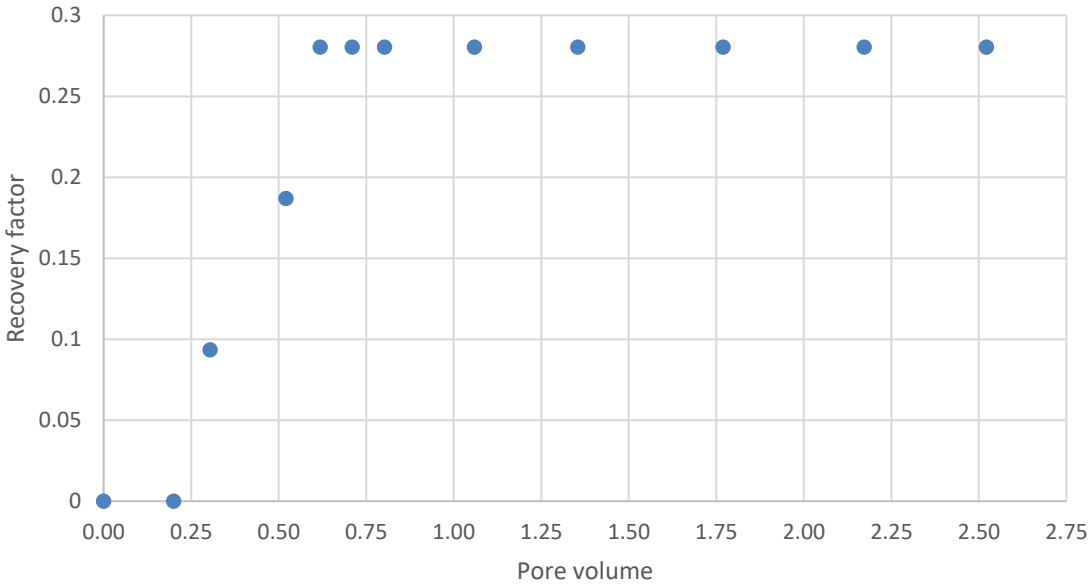

Figure 5: Waterflooding's recovery performance in exp. 1 (CO_2 gas)

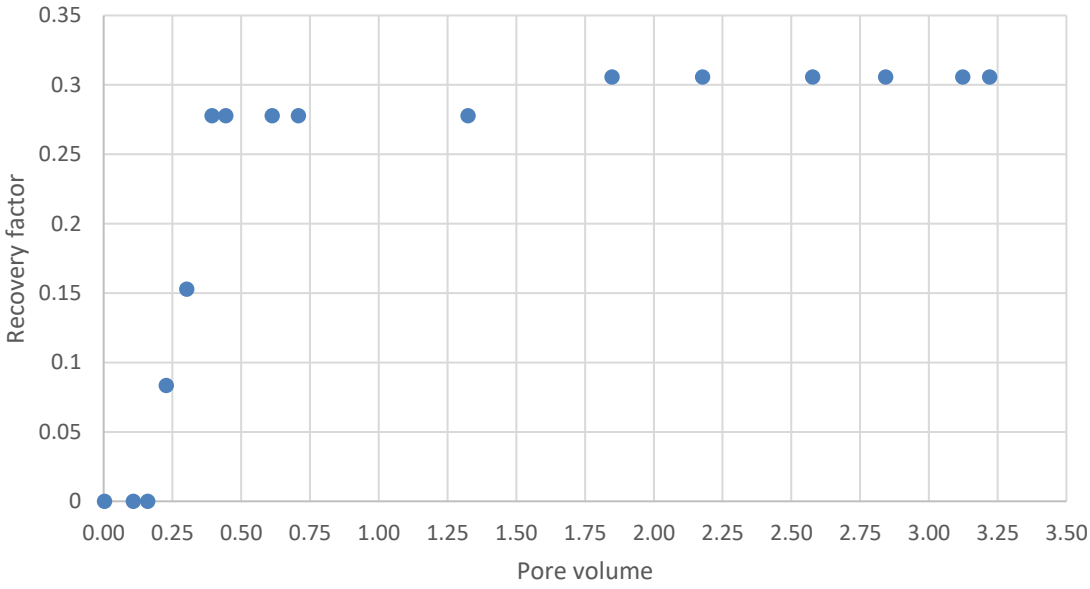

Figure 6: Waterflooding's recovery performance in exp. 2 (N_2 gas)

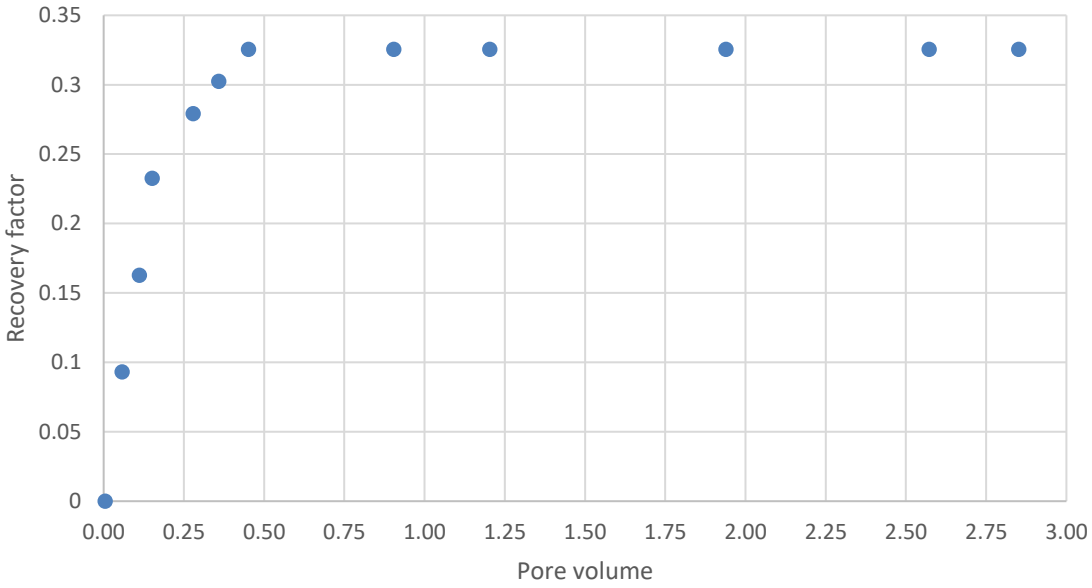

Figure 7: Waterflooding's recovery performance in exp. 3 (CO_2 foam with FS-51)

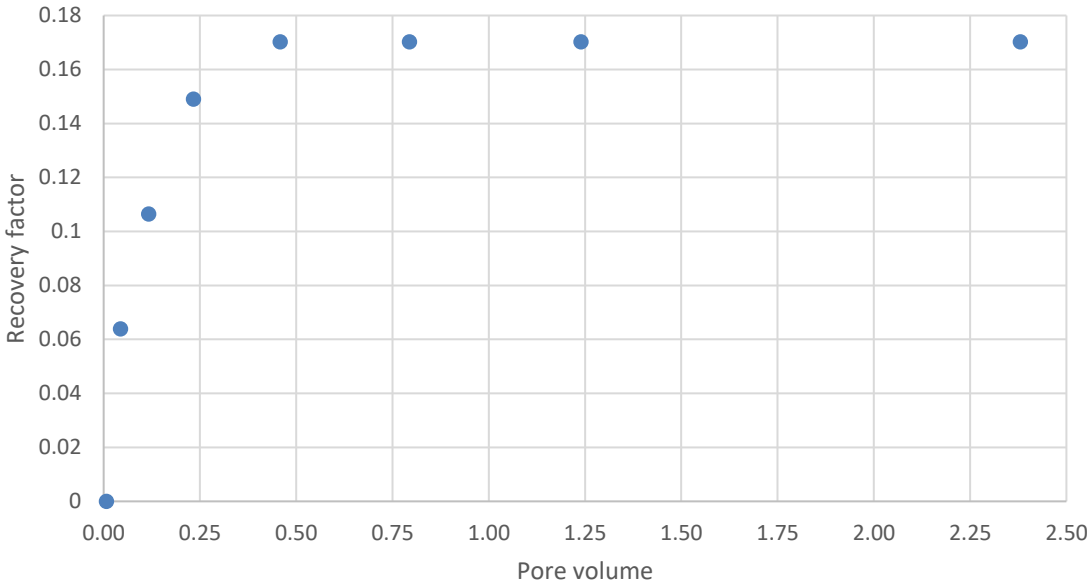

Figure 8: Waterflooding's recovery performance in exp. 4 (CO_2/N_2 foam with FS-51)

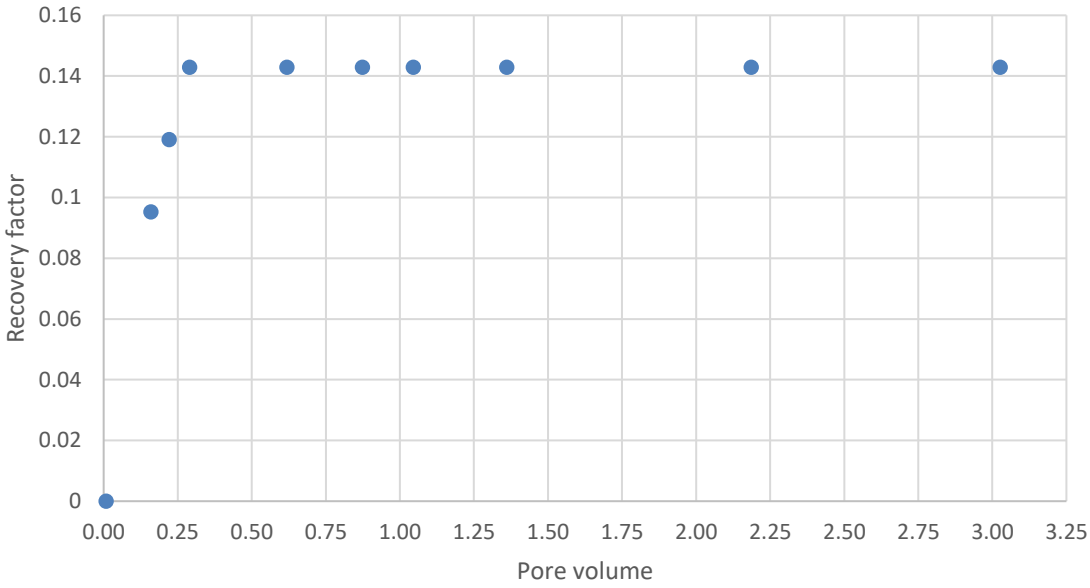

Figure 9: Waterflooding's recovery performance in exp. 5 (CO_2/N_2 foam with FS-51)

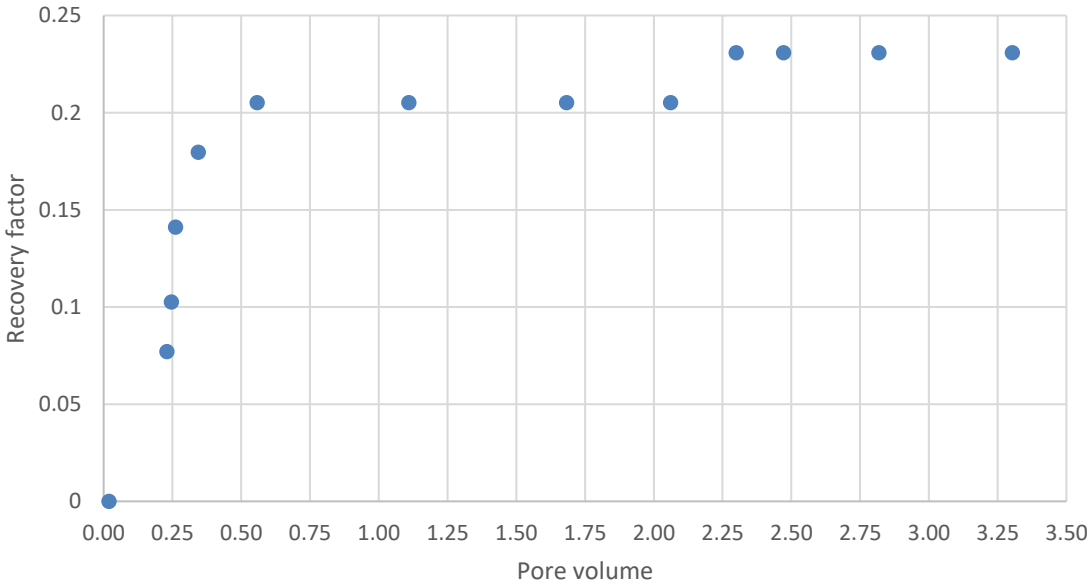

Figure 10: Waterflooding's recovery performance in exp. 6 (CO_2 foam with AOS)

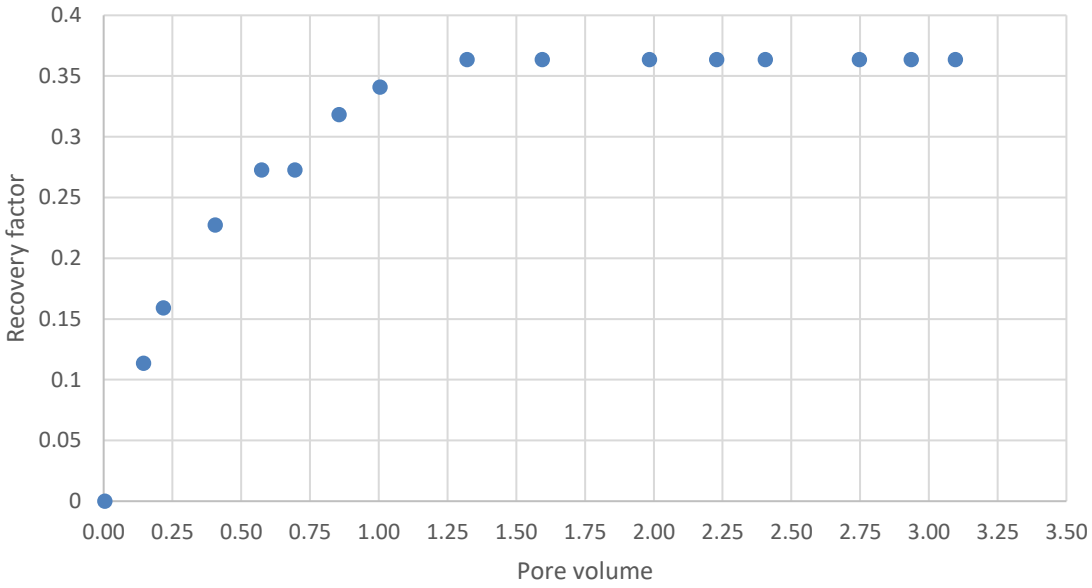

Figure 11: Waterflooding's recovery performance in exp. 7 (CO_2/N_2 foam with AOS)

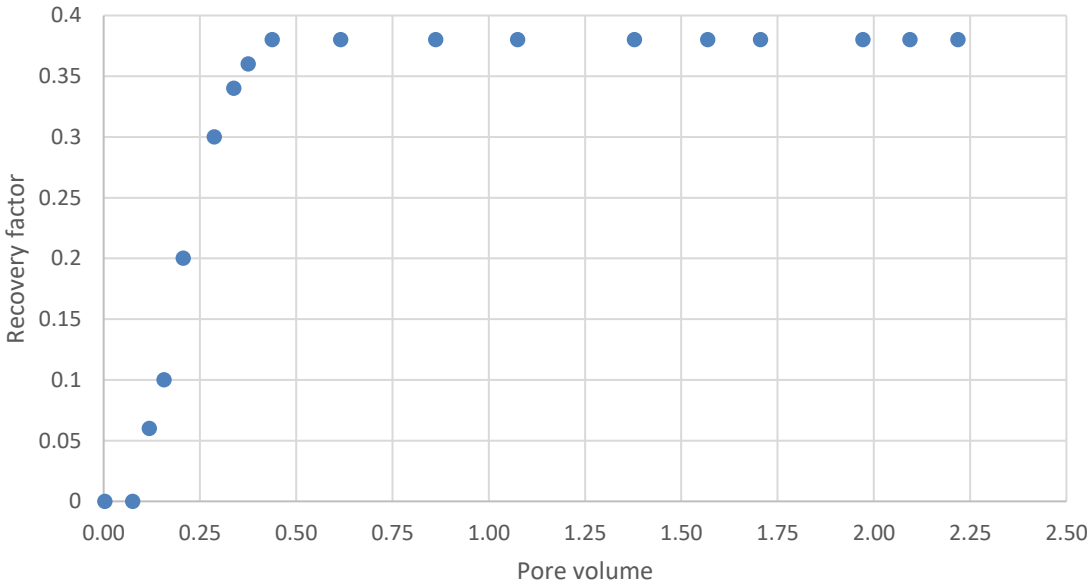

Figure 12: Waterflooding's recovery performance in exp. 8 (CO_2/N_2 foam with AOS)

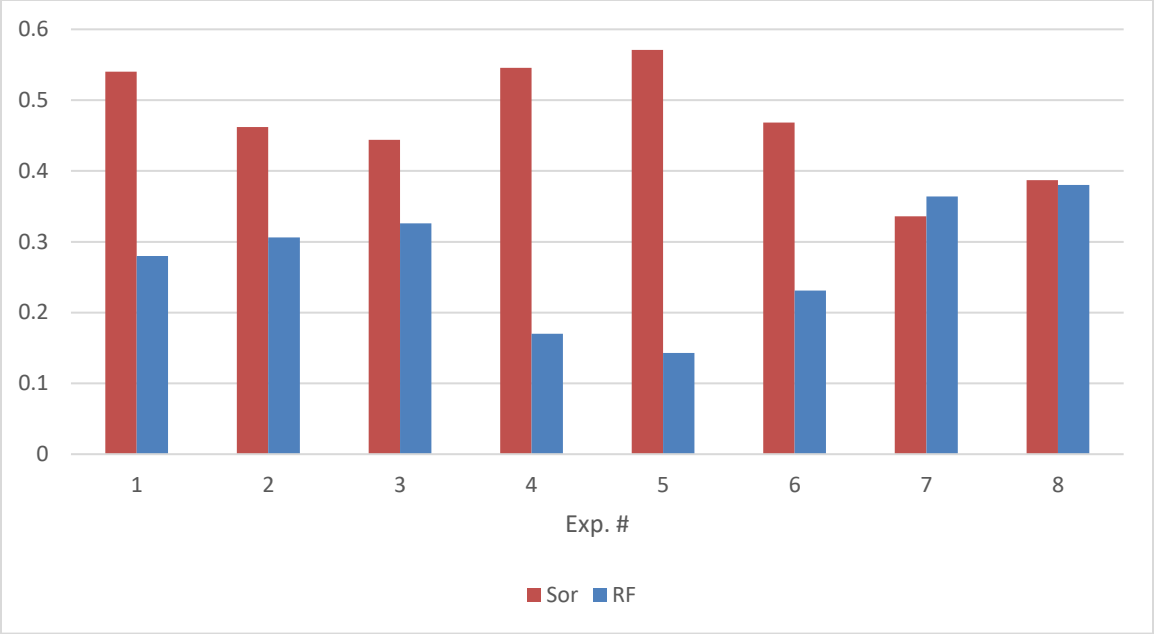

Figure 13: Summary of recovery factors and residual oil saturations for waterflooding

5.2.2 Pressure drop

Waterflooding resulted in pressure gradients across the core. Figures 14 to 21 show the pressure drop for each experiment. The way pressure varied across the core is similar in all tests. At the beginning, pressure drop increased because water was forcing the oil out of the core this increase continued until the water breakthrough, where a decline occurred in pressure drop. Then the pressure drop stabilized and reached certain value, and the remaining oil became immobile, despite injecting more water. This change in pressure drop across the core throughout the waterflooding is very common for sandstone cores [25]. Additionally, for different injection rates, conducted in experiments 1, 3, 4 & 5, the pressure drop increased at higher injection rates. Experiment 3 showed highest values for pressure drop because the core tested had the lowest permeability.

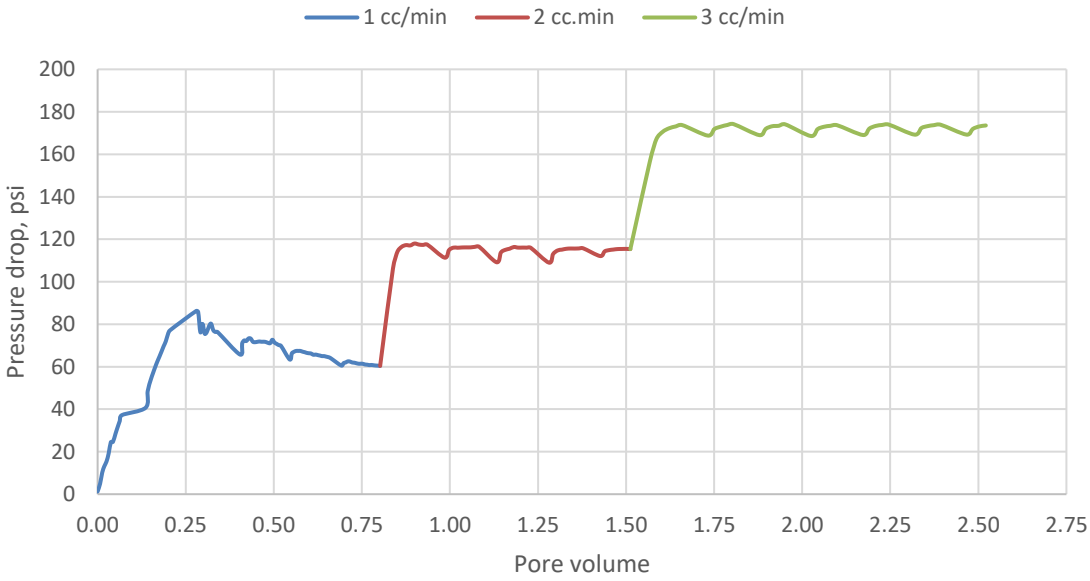

Figure 14: Pressure drop during waterflooding stage in exp. 1 (CO_2 gas)

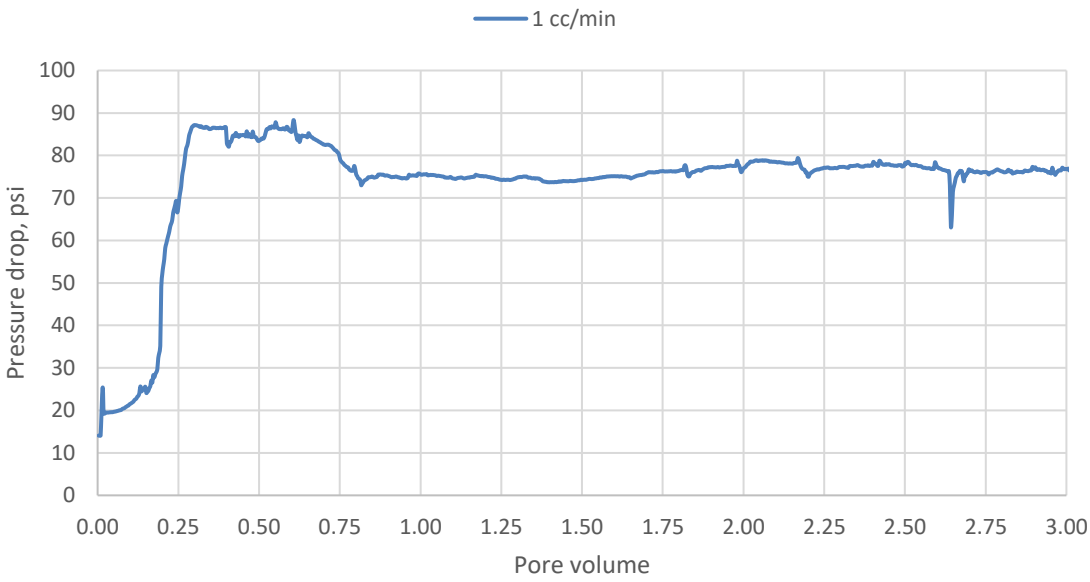

Figure 15: Pressure drop during waterflooding stage in exp. 2 (N_2 gas)

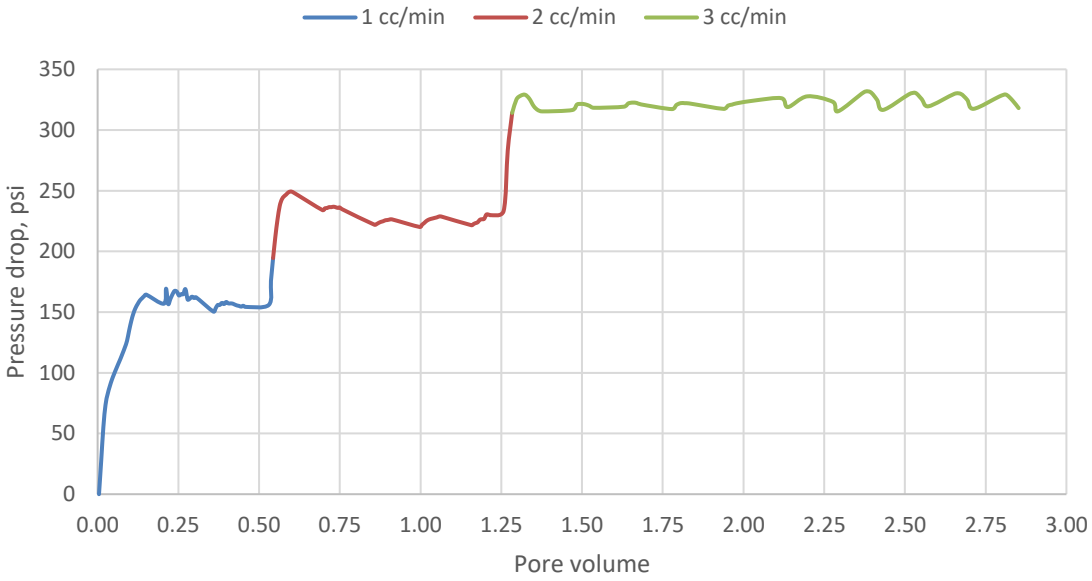

Figure 16: Pressure drop during waterflooding stage in exp. 3 (CO_2 foam with FS-51)

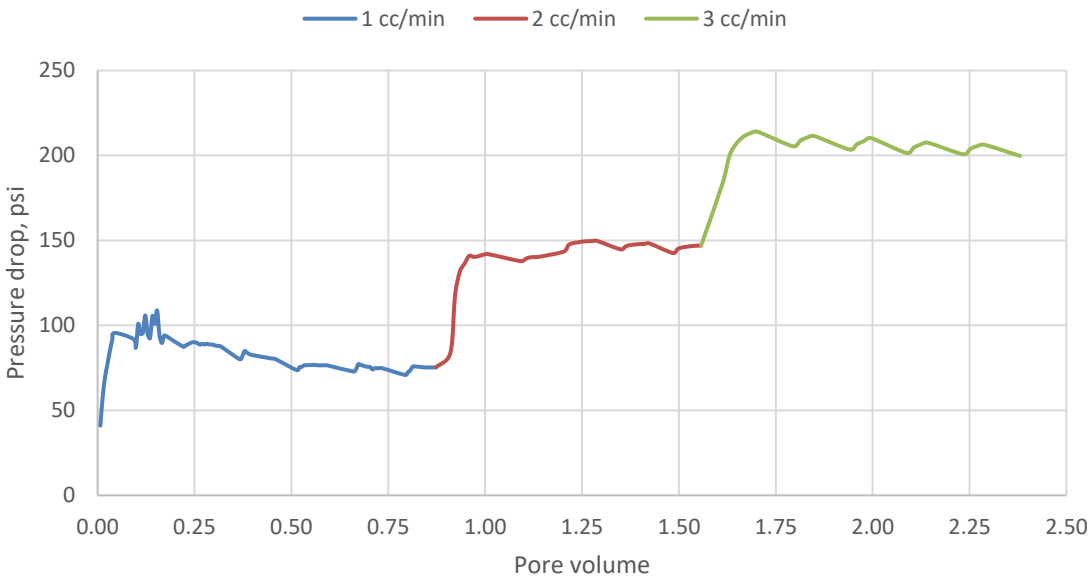

Figure 17: Pressure drop during waterflooding stage in exp. 4 (CO_2/N_2 foam with FS-51)

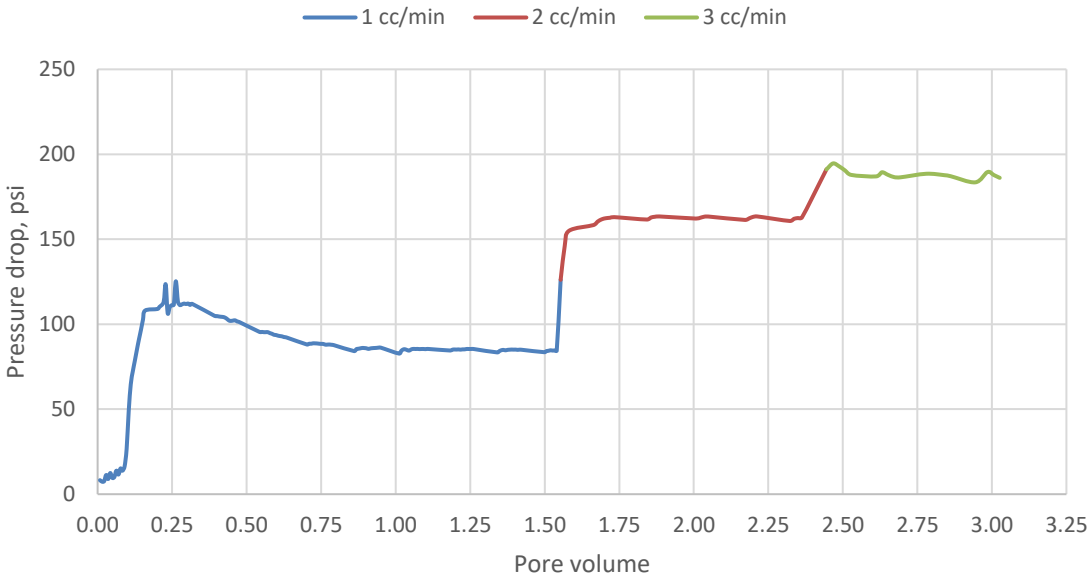

Figure 18: Pressure drop during waterflooding stage in exp. 5 (CO_2/N_2 foam with FS-51)

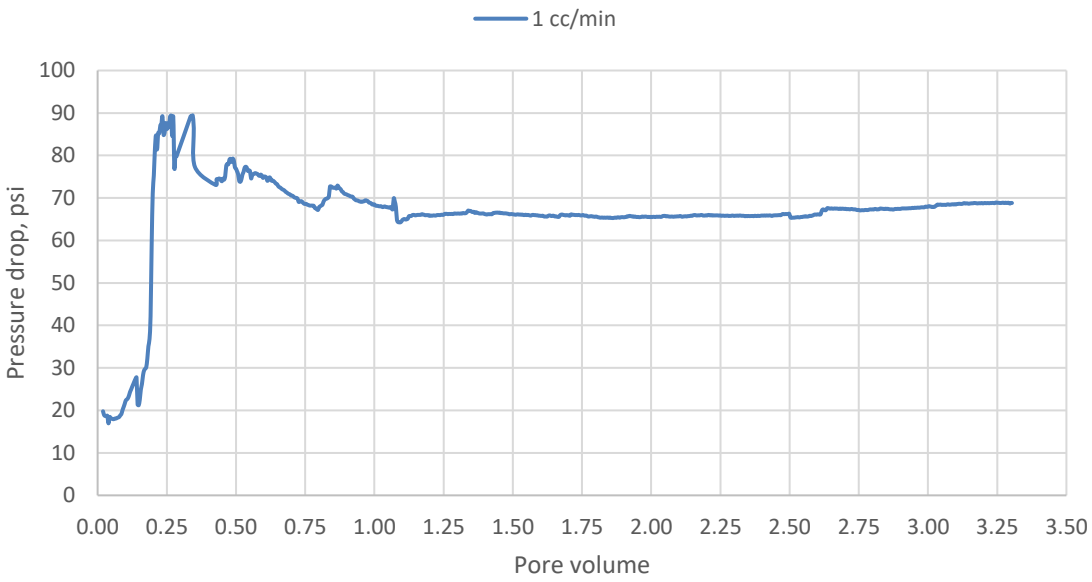

Figure 19: Pressure drop during waterflooding stage in exp. 6 (CO_2 foam with AOS)

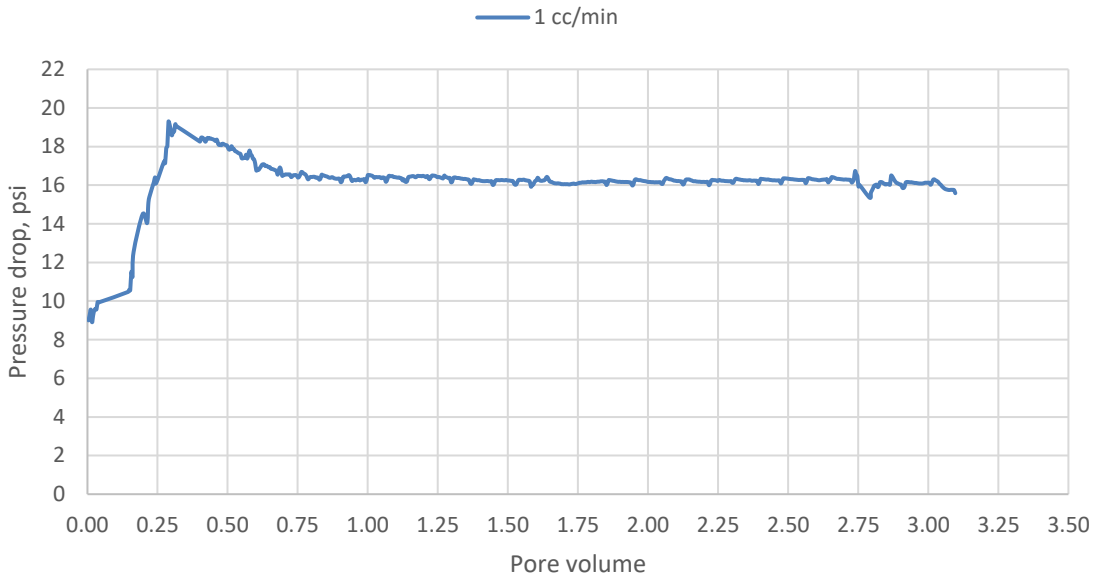

Figure 20: Pressure drop during waterflooding stage in exp. 7 (CO_2/N_2 foam with AOS)

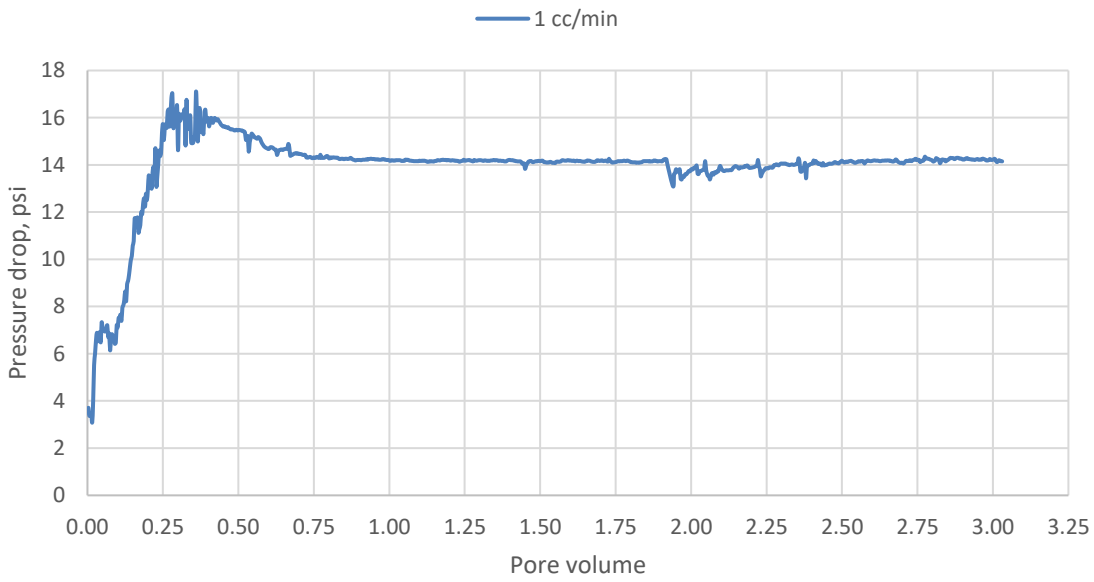

Figure 21: Pressure drop during waterflooding stage in exp. 8 (CO_2/N_2 foam with AOS)

5.3 Gas/foam flooding

5.3.1 Exp. 1: Miscible CO_2 flooding

CO_2 flooding was conducted following the waterflooding stage to recover additional oil that was not possible to be recovered by water. CO_2 was introduced into the core at pressure above the MMP to achieve miscible flooding. Back-pressure of 1700+ psi was maintained to ensure miscibility condition between n-decane and injected gases, according to Kulkami [26] and Asghari et al [27]. Basically, the miscible gas flooding is more efficient in recovering oil than the immiscible gas flooding.

Figure 22 shows the pressure drop during this stage. Like waterflooding, pressure drop kept increasing until the gas breakthrough where the pressure drop decreased considerably and then stabilized for the continuing injection of CO_2. Increase of differential pressure before breakthrough is due to high compressibility of gas. After breakthrough gas has an open path to flow and with increasing gas saturation, gas relative permeability increased and differential pressure decreased [28]. The gas breakthrough occurred close to 0.2 PV injected, which is relatively early in comparison to other forms of tertiary recovery. This can be contributed also to the high permeability in this core (97.54 md). After 1 PV injection of CO_2 the rate was increased from 1 to 2 cc/min, which resulted in slight increase in the pressure drop. Figure 23 shows the recovery performance in this stage.

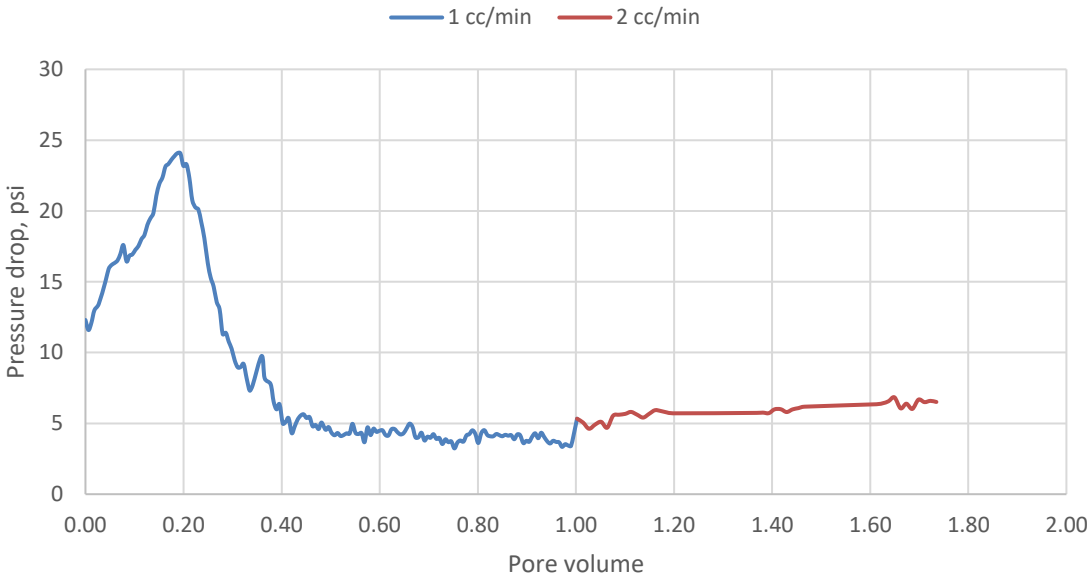

Figure 22: Pressure drop during CO_2 flooding in exp. 1

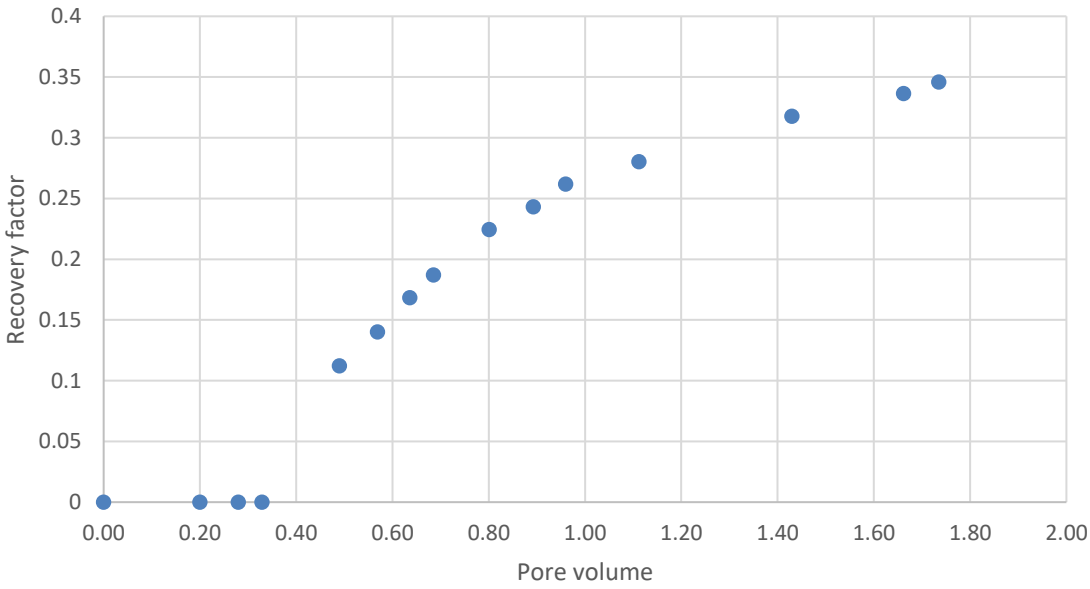

Figure 23: Recovery performance during CO_2 flooding in exp. 1

5.3.2 Exp. 2: N_2 flooding

In this experiment N_2 was injected, in an immiscible mode, as an EOR agent to recover the left-behind oil after the waterflooding stage. The resulting recovery factor of oil by N_2 injection was 40%. When compared to 48.1% of oil recovery achieved by the miscible CO_2 flooding (exp. 1), it is postulated that it was due to the preferable characteristics of CO_2, as mentioned earlier. Figure 24 shows the recovery performance during N_2 injection. According to Ghoodjani1 and Bolouri [28], CO_2 has higher capability, than N_2, to reduce the interfacial tension and oil viscosity and to reduce the residual oil saturation by swelling mechanism, thus higher recovery factor in CO_2 flooding than N_2.

As for the pressure differential across the core during the N_2 injection, the pressure drop (or pressure differential) was increasing at the beginning and then decreased steadily before stabilizing all the way to the end of N_2 flooding. The gas breakthrough occurred early at nearly 0.2 PV of flooding, which was similar to the time of breakthrough in the miscible CO_2 flooding (exp. 1). Thus, the trend of the pressure differential in N_2 flooding looked like the trend in the case of CO_2 flooding.

However, the pressure drop recordings indicated higher pressure gradient in the case of N_2 flooding than that in the case of CO_2 flooding. Several factors might have contributed to this finding: 1) In exp.1 (CO_2 flooding), the relative permeability was higher, the oil viscosity was lower, and the interfacial tension was lower, because of the interaction mechanisms took place between the injected CO_2 and oil-in-place, compared to exp. 2 (N_2 flooding). 2) The differential pressure during CO_2 flooding was lower due to the higher solubility of CO_2 in oil [28]. 3) The absolute permeability of core used in exp. 2 (N_2

flooding) was lower than that of exp. 1 (CO_2 flooding). Figure 25 shows the pressure drop during the N_2 flooding.

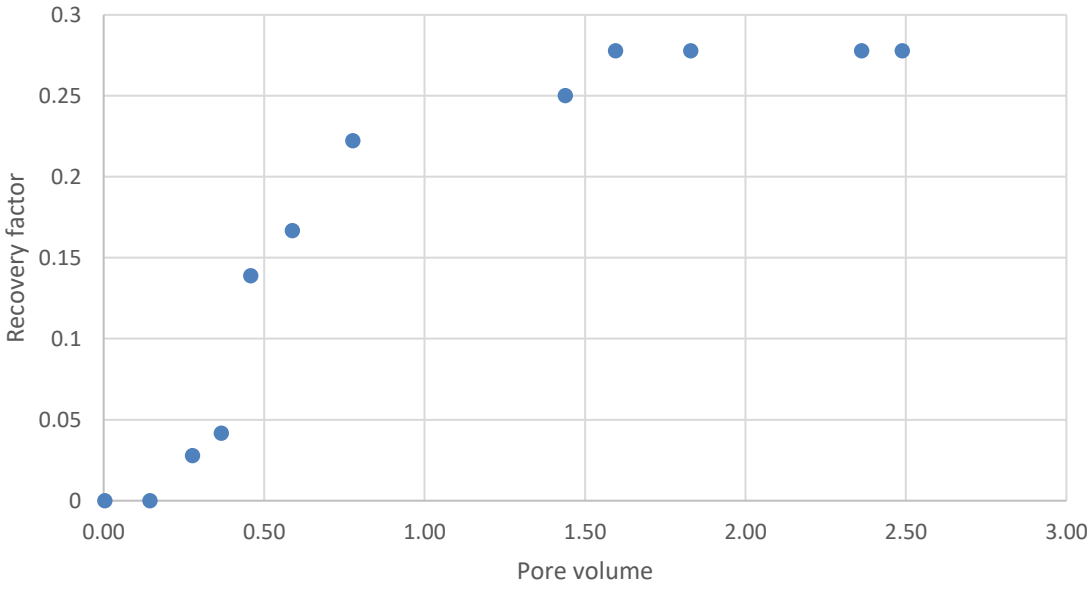

Figure 24: Recovery performance during N_2 flooding in exp. 2

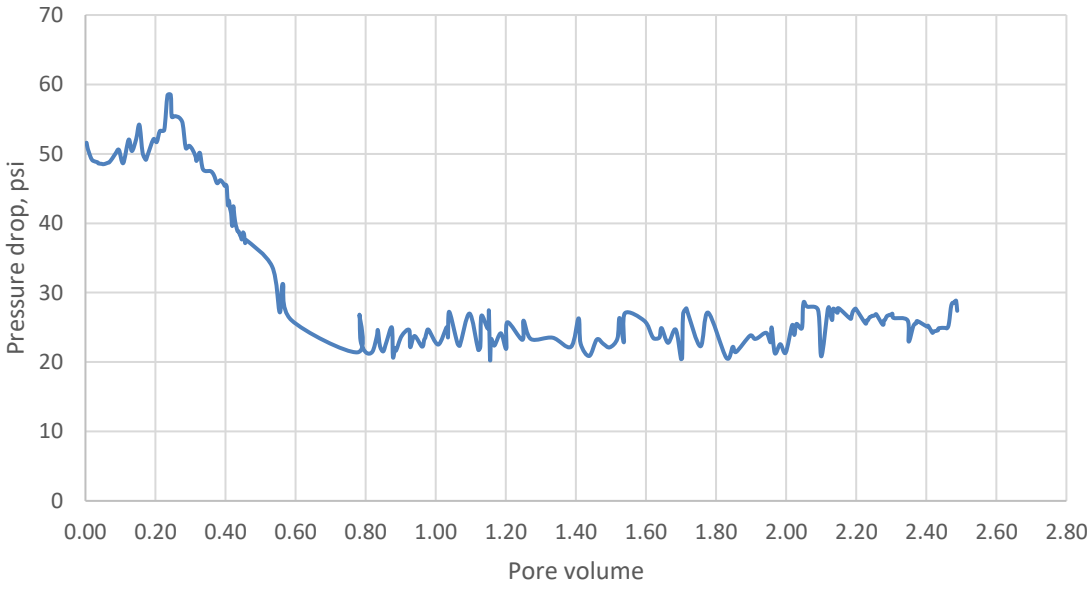

Figure 25: Pressure drop during N_2 flooding in exp. 2

5.3.3 Exp. 3: CO_2 foam flooding with fluorosurfactant (FS-51)

In experiment 3 and following the waterflooding, CO_2 gas and FS-51 surfactant solution (0.15 vol%) were injected simultaneously to generate an in-situ foam, with a foam quality of 80%. At first, the CO_2 injection rate was 0.8 cc/min and for the surfactant it was 0.2 cc/min, thus the total foam injection rate equaled 1 cc/min. Then after injecting 1.2 PV of foam, the CO_2 and surfactant' injection rates were doubled to be 1.6 and 0.4 cc/min respectively, resulting in total foam injection rate of 2 cc/min, as shown in Figure 26.

Following the start of foam flooding, no oil was produced at early times. Then, oil started to be produced after injecting 0.5 PV of foam. Oil production continued for about two more pore volumes of foam injection. After that, oil ceased to show up at the recovery tube despite injecting one more pore volume of foam, as shown in Figure 27. However, the recovery factor by CO_2 foam flooding was 69%. The miscible CO_2 flooding (exp. 1) recovered 48% of the remaining oil after waterflooding. Thus, the foam flooding improved the oil recovery, when compared to oil recovery by CO_2. The gas bubbles started to appear at the recovery tube after the injection of 0.7 PV of foam, indicating the occurrence of gas breakthrough. The foam generation was effective in delaying the gas breakthrough and allowing for gas to cover more areas inside the core.

Looking at the pressure drop behavior (Figure 26), It is postulated that increasing the injection rate caused the foam bubbles to collapse, which rendered the decrease in pressure drop after 2 PVs of foam injection. Afterwards, foam started to generate again and pressure drop started to rise. Further injection of foam would keep the pressure drop rising as oil saturation would decrease. The lower the oil saturation, the higher the pressure drop across the core.

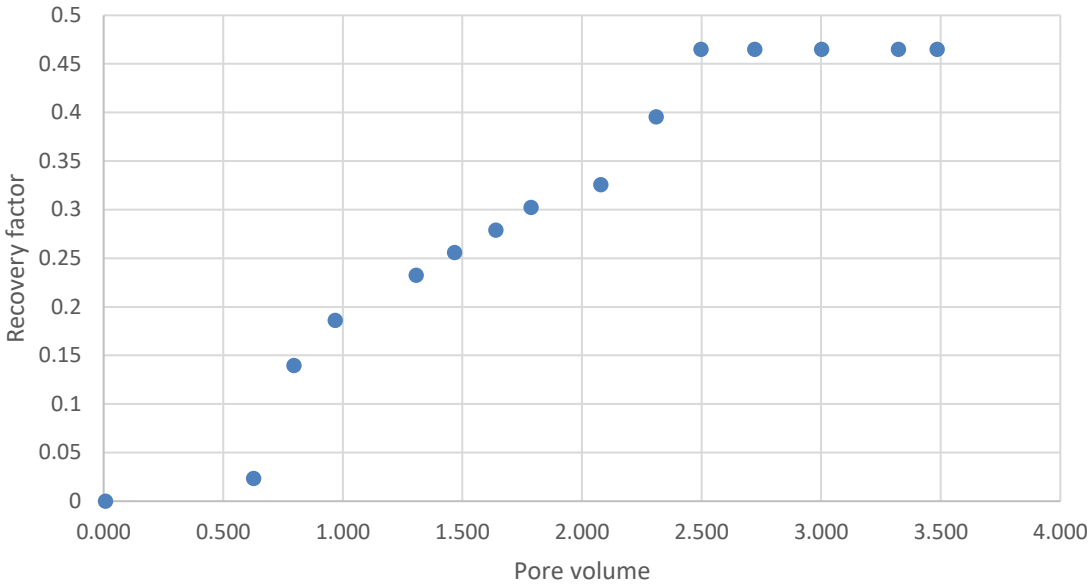

Figure 26: Recovery performance during CO_2 foam flooding in exp. 3

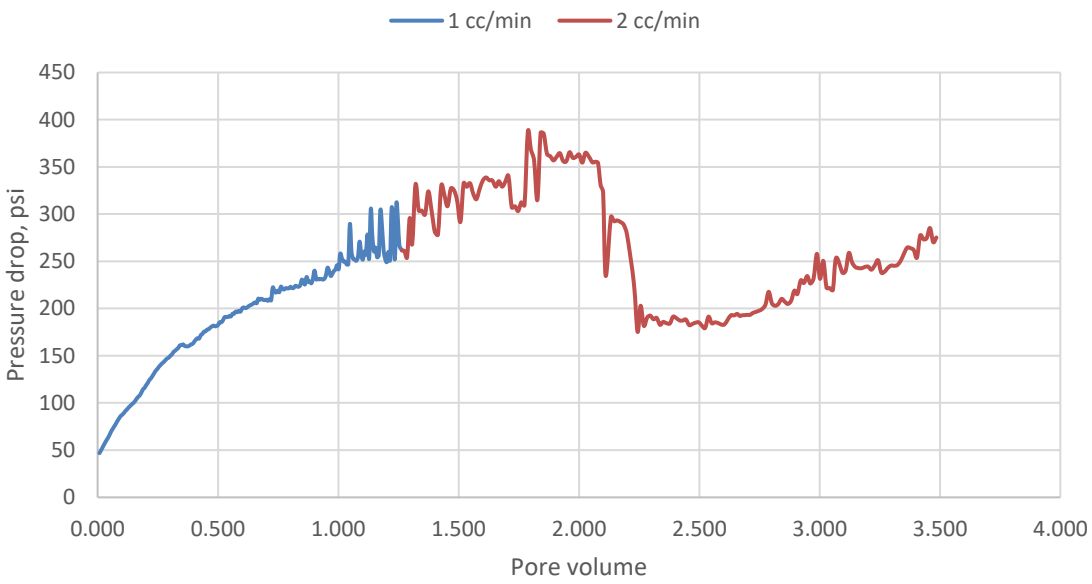

Figure 27: Pressure drop during CO_2 foam flooding in exp. 3

5.3.4 Exp. 4: CO_2/N_2 foam flooding with fluorosurfactant (FS-51)

In this experiment, CO_2, N_2, and FS-51 surfactant solution were injected into the core simultaneously to generate the foam, with a foam quality of 80%. The gaseous phase consisted of CO_2 and N_2 with 80:20% volume ratio. Firstly, the injection rates for CO_2, N_2, and FS-51 were 0.64, 0.16 and 0.2 cc/min, making the 1 cc/min of total foam injection rate. Then after flooding 1.3 PV of foam, the injection rates for CO_2, N_2, and FS-51 were doubled to be 1.28, 0.32 and 0.4 cc/min, the resulting total foam injection rate became 2 cc/min.

Oil production (n-decane) started after flooding nearly 1 PV of foam. Also, the gas breakthrough took place at 0.9 PV, as shown in Figure 28. The oil recovery by CO_2/N_2 foam was 51%, it was 69% CO_2 foam (exp. 3). The reason for the lower recovery is the addition of N_2 in a small amount to CO_2 because CO_2 is more soluble in oil than N_2. The presence of N_2 would reduce CO_2 solubility in oil. However, the recovery performance by this foam mixture remained better than the performance by CO_2 gas (exp. 1).

As for the pressure drop (Figure 29), it showed gradual increase in the pressure drop as the flooding continued. Again, further sweep of the core with foam would recover more oil and decrease oil saturation, and increase the surfactant saturation. Thus, foam would be more stable inside the core and be generated in larger volumes.

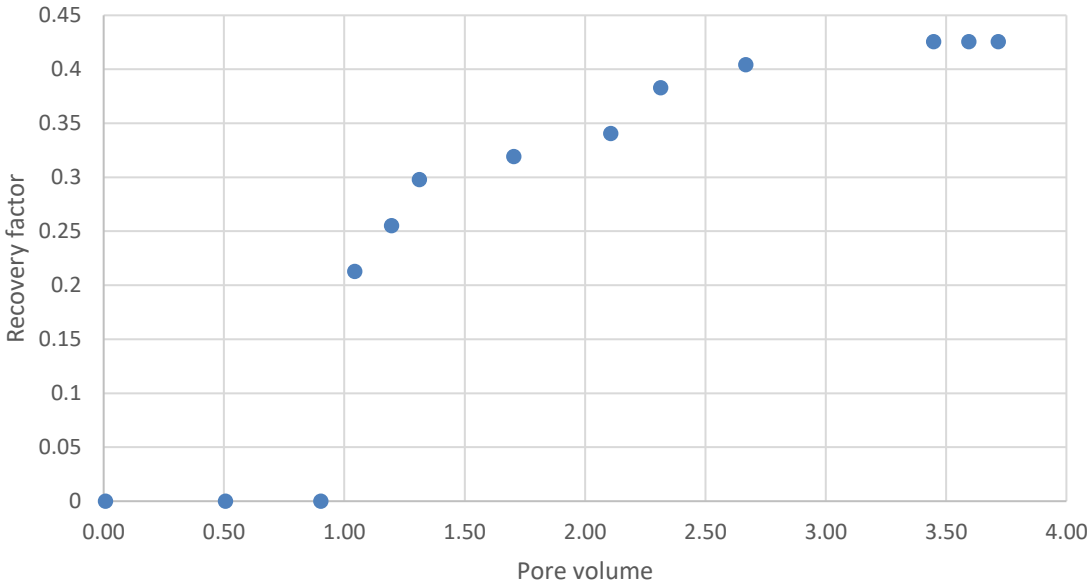

Figure 28: Recovery performance during CO_2/N_2 foam flooding in exp. 4

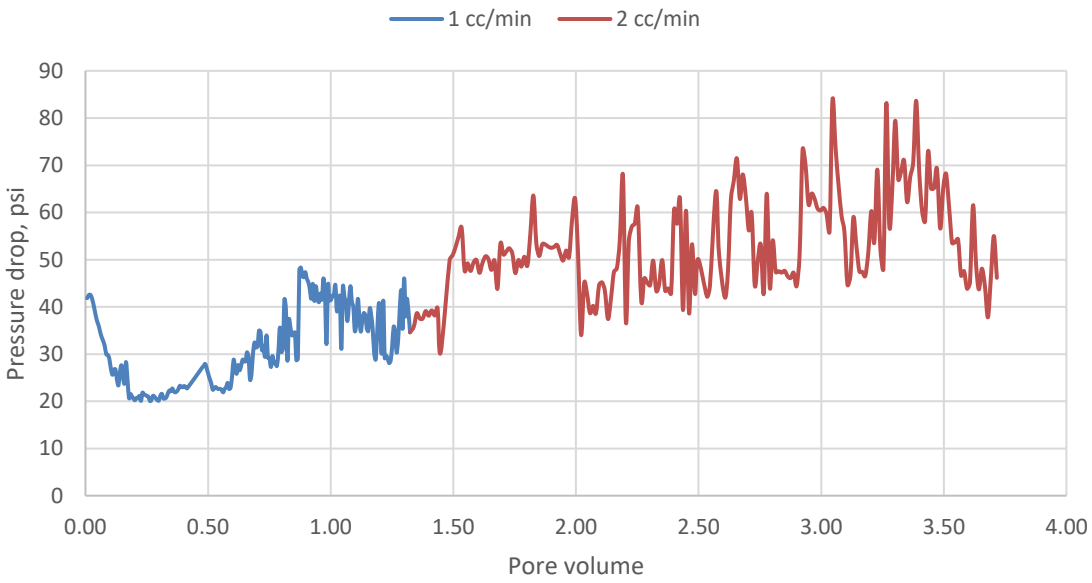

Figure 29: Pressure drop during CO_2/N_2 foam flooding in exp. 4

5.3.5 Exp. 5: CO_2/N_2 foam flooding with fluorosurfactant (FS-51)

In the fifth experiment, CO_2, N_2, and FS-51 solution were all injected simultaneously. The foam quality was raised to be 90%. Firstly, the injection rates for CO_2, N_2, and FS-51 were 0.72, 0.18 and 0.1 cc/min, making the 1 cc/min of total foam injection rate. Then after flooding 1.6 PV of foam, the injection rates for CO_2, N_2, and FS-51 were doubled to be 1.44, 0.36 and 0.2 cc/min, the resulting total foam injection rate became 2 cc/min.

The oil recovery resulted from this experiment was 50%. This percentage was slightly higher than the CO_2 gas in exp. 1 (48%), lower than the CO_2 foam in exp. 3 (69%), but nearly the same as the CO_2/N_2 foam with 80% foam quality as in exp. 4 (51%). As Figure 30 illustrates, the oil recovery began only after the injection of 1.2 PV of foam. The gas breakthrough occurred after injecting 1.3 PV of foam into the core.

The trend in pressure drop was almost stable up until 2.2 PV of foam injection. Then the pressure drop started to rise considerably, as more oil was being produced and replaced by more volumes of surfactant inside the core pores. In comparison to exp. 4 (CO_2/N_2 foam with 80% foam quality), the pressure differential across the core in exp. 5 was lower. According to Siddiqui's findings [29], the steady-state pressure drop at 80% foam quality is higher than the steady-state pressure drop at 90% for Fluorosurfactant. Figure 31 shows the pressure drop in this flooding test.

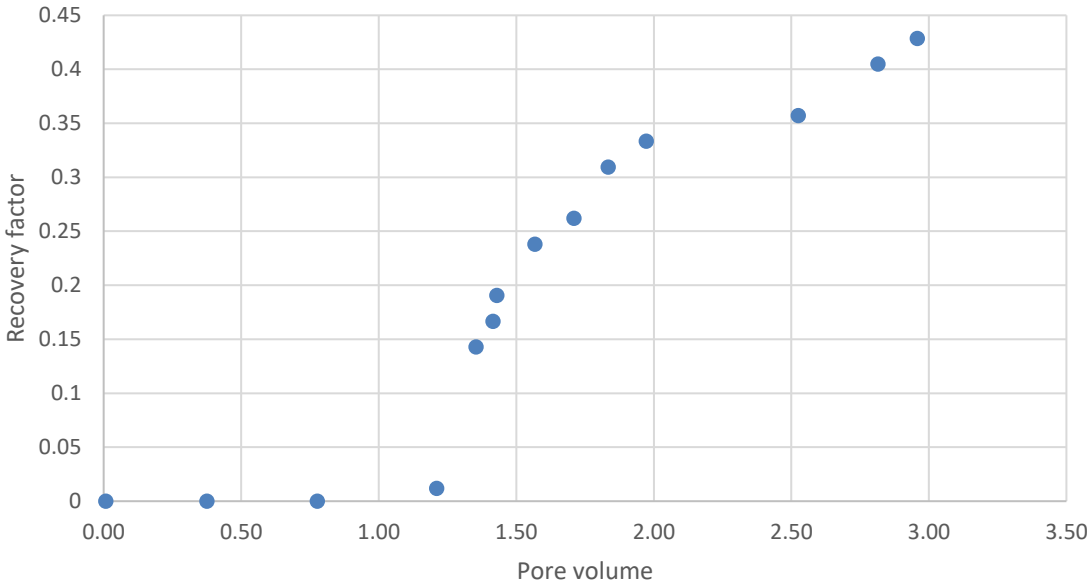

Figure 30: Recovery performance during CO_2/N_2 foam flooding in exp. 5

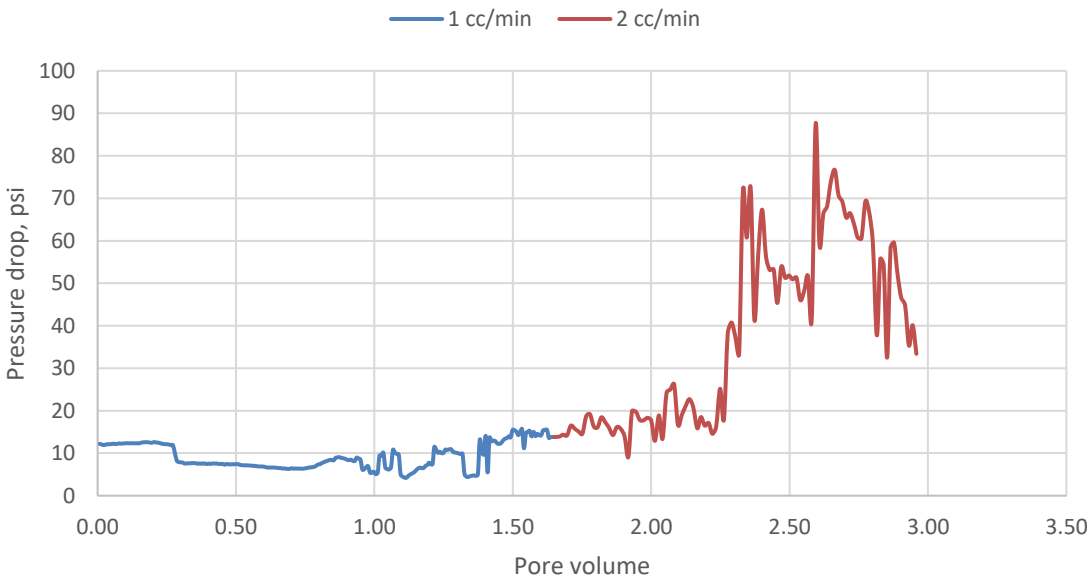

Figure 31: Pressure drop during CO_2/N_2 foam flooding in exp. 5

5.3.6 Exp. 6: CO_2 foam flooding with AOS

Foam was generated using AOS (with a concentration of 0.5% vol) as a foaming agent in this experiment, with a foam quality of 80%. The injection rate of CO_2 was 0.8 cc/min and for AOS solution it was 0.2 cc/min. So, only one foam injection rate was used, 1 cc/min.

The ultimate recovery factor after conducting the foam flooding was 66.7%, in comparison to an ultimate recovery factor of only 48% when pure CO_2 gas was used in experiment 1. This comparison shows the benefit of foaming the injected gas to recover more oil. Figure 32 shows the recovery performance of experiment 6. However, CO_2 foam with FS-51 (exp. 3) recovered 69% of oil, which is slightly more than the recovery factor resulted from CO_2 foam with AOS (exp. 6). The gas breakthrough happened after the injection of 0.8 PV of foam. Earlier in other test when foam was generated by CO_2 and FS-51 (exp. 3), the gas breakthrough occurred after the injection of 0.7 PV of foam. Thus, the change in the foaming agent did not affect much the time of gas breakthrough.

The pressure drop across the core during the foam injection was very high (Figure 33). The pressure drop after the injection of 1 PV of foam was increasing rapidly suggesting the possibility of pores plugging by fines migration of inside the core. Pressure differential as high as 1000 psi cannot be attributed to foam generation solely. However, the oil production continued after 1 PV of foam injection.

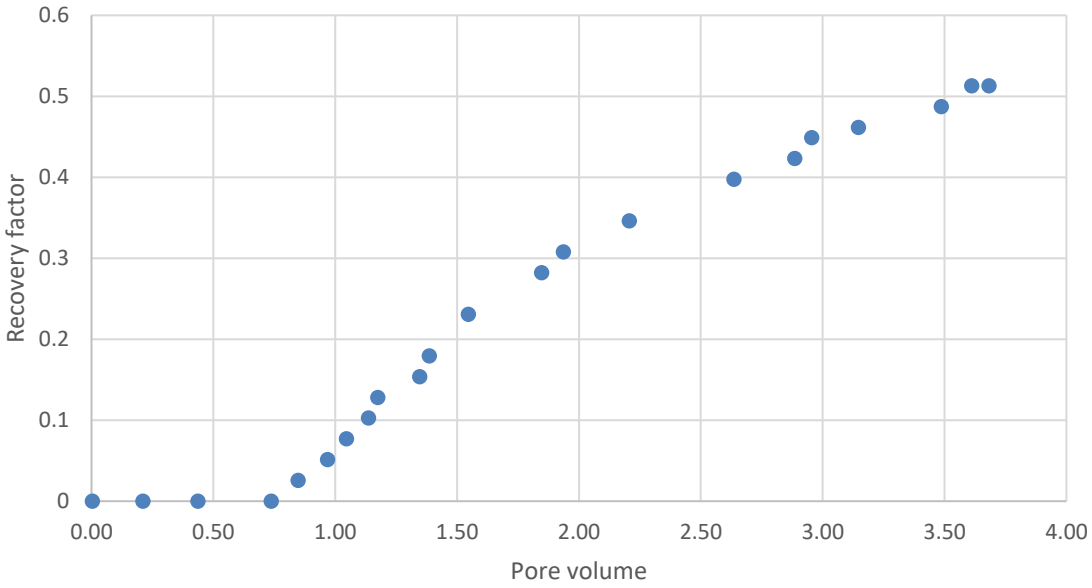

Figure 32: Recovery performance during CO_2 foam flooding in exp. 6

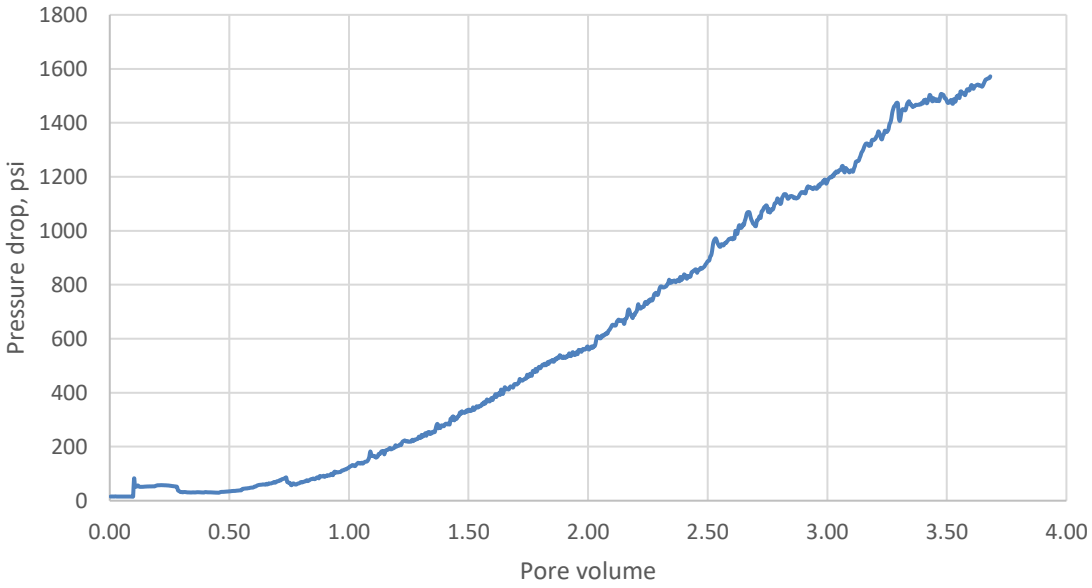

Figure 33: Pressure drop during CO_2 foam flooding in exp. 6

5.3.7 Exp. 7: CO_2/N_2 foam flooding with AOS

In this experiment, N_2 was mixed with CO_2 with a percentage of 20%. The foam quality used was 80%. Like experiment 4 where the foam mixture composed of CO_2, N_2 and FS-51, the volume ratio of CO_2 and N_2 used in this test was 80:20%. The injection rates for CO_2, N_2, and AOS were 0.64, 0.16 and 0.2 cc/min, making the 1 cc/min of total foam injection rate.

The foam flooding following the waterflooding achieved 77.3% of ultimate oil recovery. This is higher than the ultimate recovery gained by the AOS-foamed CO_2 (exp. 6) which was 74.4%. However, the waterflooding in experiment 7 performed better than in experiment 6, which resulted in the enhancement in ultimate recovery. Figure 34 shows the recovery performance in experiment 7. The gas breakthrough took place at 0.8 PV of foam injection.

The pressure drop graph (Figure 35) shows stable pressure drop after the breakthrough for almost 1 PV before increasing rapidly to reach 200 psi at the end of experiment. The increasing pressure drop reflects the growing flow resistance of injected fluid due to the increase of foam saturation replacing the produced oil.

In comparison to experiment 4 where FS-51 was the foaming agent, AOS generated higher pressure drop across the core, which indicated its better foaming effect.

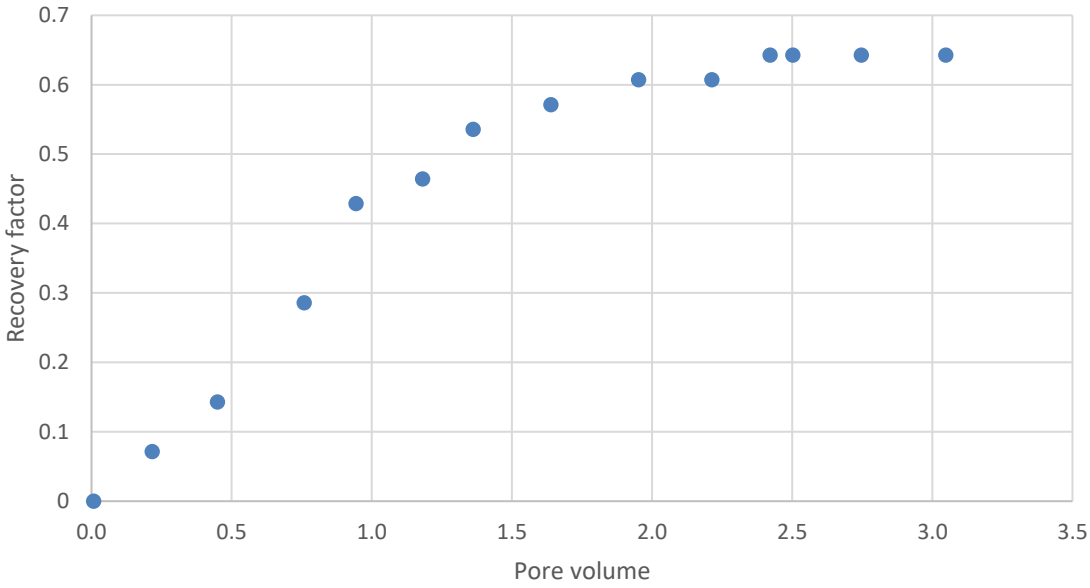

Figure 34: Recovery performance during CO_2/N_2 foam flooding in exp. 7

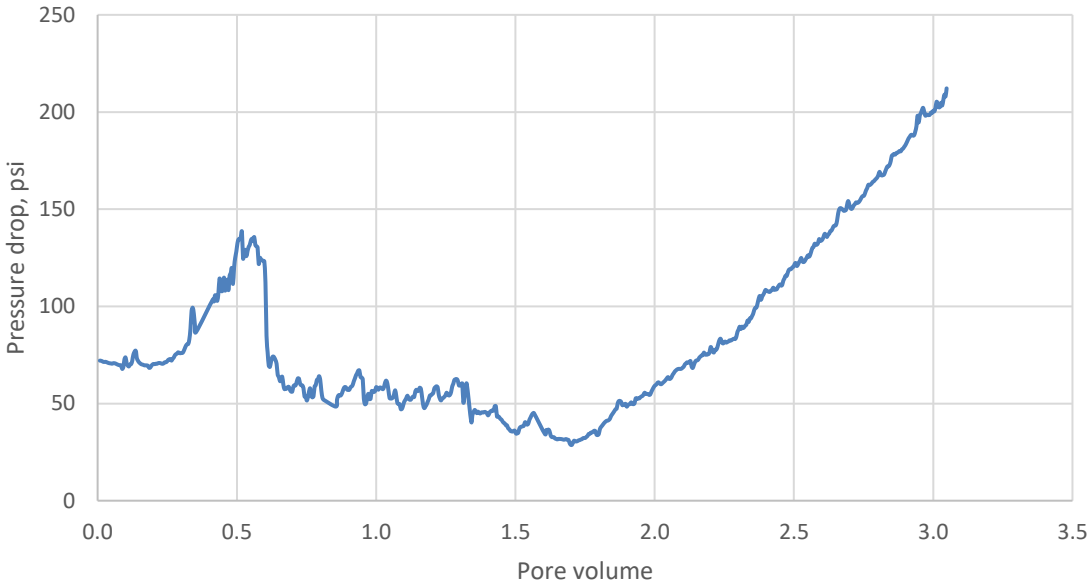

Figure 35: Pressure drop during CO_2/N_2 foam flooding in exp. 7

5.3.8 Exp. 8: CO_2/N_2 foam flooding with AOS

In this experiment, foam quality was 90%, and N_2 fraction was 20% in the CO_2/N_2 mixture. The total foam injection rate was 1 cc/min consisting of 0.72 cc/min for CO_2, 0.18cc/min of N_2, and 0.1 cc/min of AOS, like the case in experiment 5 except the FS-51 was the foaming agent.

Unlike the other foam flooding tests, the oil production started almost quickly after the beginning of foam injection. Also, the gas breakthrough did not take much time to occur. The ultimate oil recovery in this experiment was 78%, like the ultimate recovery in the previous test (exp. 7) when it was 77.3%. It indicated that change in foam quality did not affect much on the performance of oil recovery (Figure 36).

Similarly, the pressure drop in this experiment has the same range as the previous test. Figure 37 shows the pressure drop response in experiment 8. Looking at the pressure drop behavior in almost all the foam tests, it can be seen the similarity in the foam behavior with respect to the pressure drop. Foam was being injected to help recover the oil and, while doing that, the oil saturation was decreasing. More surfactant was entering the core and staying inside the pores allowing for generating more stable foam. This behavior was reflected on the pressure drop graph where rapid increase in the pressure differential all the way to the end of foam flooding.

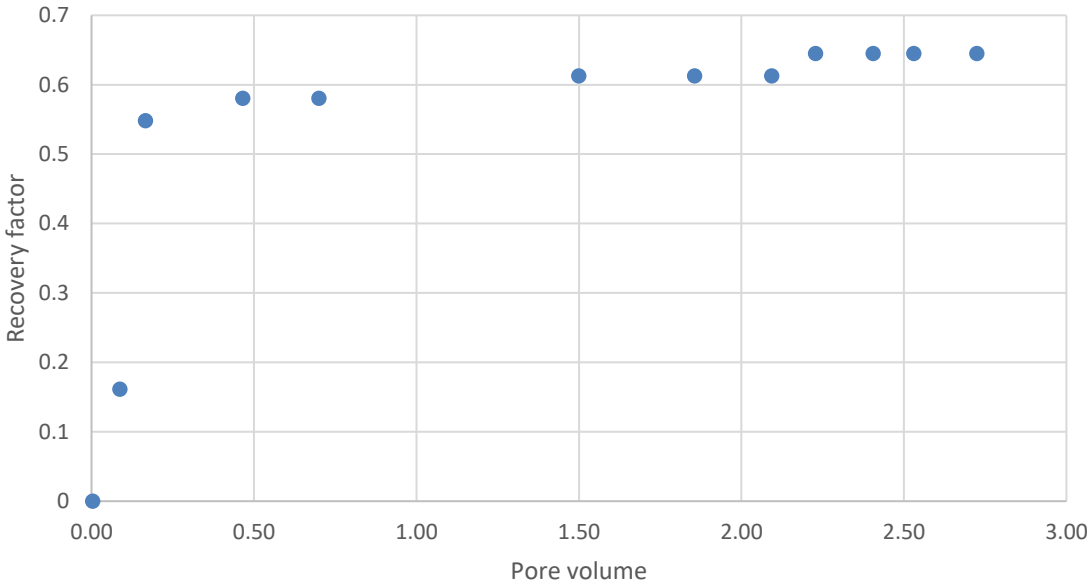

Figure 36: Recovery performance during CO_2/N_2 foam flooding in exp. 8

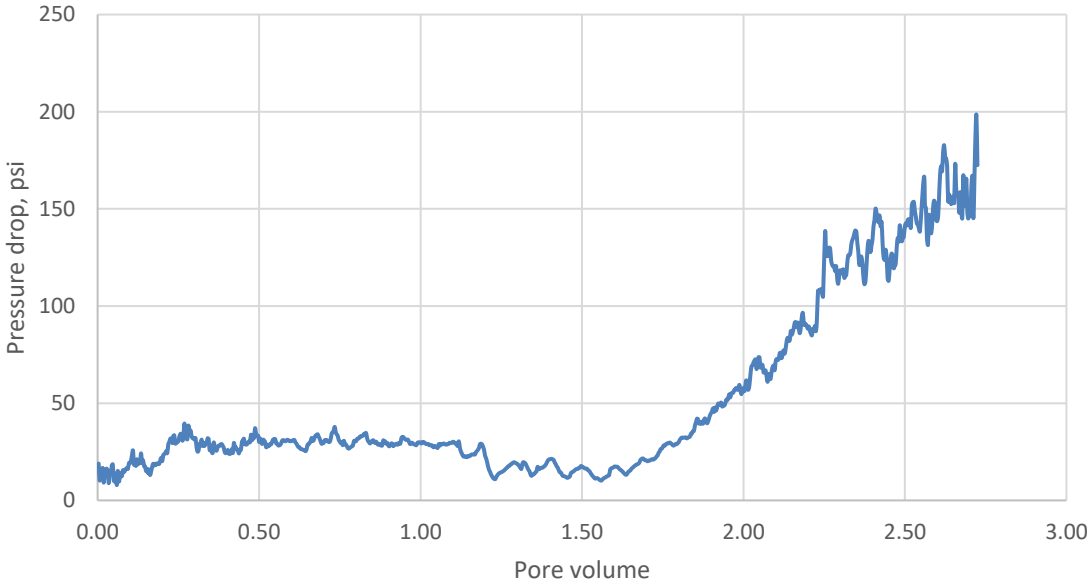

Figure 37: Pressure drop during CO_2/N_2 foam flooding in exp. 8

CHAPTER 6

CONCLUSIONS AND RECCOMENDATIONS

The goal of this research was to investigate the performance of foam flooding in Enhanced Oil Recovery. More specifically, to assess the performance of foam mixtures composed of carbon dioxide, nitrogen and two different types of surfactants. The study factors included the recovery factor: how much oil can be recovered after the waterflooding? and the pressure drop: to which extent the foam could reduce the mobility of injected gases?

The novel mixture of foam used in this research had been formulated in previous studies based on foam stability tests and foam texture characterization. Theses formulated foam mixtures had given the most stable foam behavior and strength. It is well-known that foam stability is the most important element to ensure the success of any EOR foam flooding.

To generate foam, a foaming agent (surfactant) and gas are mixed together. In EOR applications, carbon dioxide is the most used gas to generate a stable foam in sandstone or carbonate formations. However, the ability of CO_2 at supercritical condition is reduced to make a stable foam, thus jeopardizing its usefulness. To solve this problem, N_2 was added in small fraction to CO_2 to study its effect on the stability of foam [29]. Though, the novel mixture of foam consisting of CO_2 and N_2 had not been tested on oil recovery.

In this research, different EOR schemes were investigated and they involved the miscible CO_2 flooding, the immiscible N_2 flooding, CO_2 foam flooding, and CO_2/N_2 foam flooding. two types of surfactant were used: fluorosurfactant (FS-51) and Alpha-olefin-sulfonate

(AOS). The coreflooding tests were conducted at CO_2 supercritical conditions. The analysis of the results from the coreflood tests can be concluded in the following:

- Foaming the injected gases succeeded in lowering the mobility of the injected gases which helped in contacted more areas inside the core. Eventually, the oil recovery by the foam flooding was better than by the pure gas flooding.
- The addition of N_2 to CO_2 in foam mixtures did not show any improvement in terms of oil recovery. In other words, CO_2 foam flooding recovered more oil than CO_2/N_2 foam flooding. Also, miscible CO_2 flooding achieved more oil recovery than N_2 flooding. CO_2 has better displacement characteristics than N_2, and adding N_2 to CO_2 would reduce the displacement efficiency of CO_2.
- The variation in foam quality did not change much the foam behavior.
- FS-51 when used as a foaming agent proved its capability to generate foam in the high-salinity environment.

This research has given many useful outcomes. These outcomes may help to further understand the behavior of foam inside the core. For the future work many recommendations can be suggested:

- To change the flooding strategy from the co-injection mode to the alternative injection of gas and surfactant (SAG).
- To investigate phase behavior of the injected gases and surfactant when come in contact with the oil in place. The study of phase behavior is useful to give better understanding of the interactions that takes place on a molecular level.

- To introduce the technique of visualized testing during the coreflooding is thought to be helpful in tracing the flood fronts and the contacted region inside the core by the foam.
- Finally, the evaluation of coreflooding results should be done while keeping all the parameters consistent. Theses parameters include the core characteristics, the injection conditions, the injection fluids' properties, etc.

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APPENDIX

First stage of coreflooding involved the injection of formation brine into the core. The brine injection was done at three different injection rates. Each injection rate resulted in stabilized pressure drop across the core. The following Figures (38-45) shows the pressure drop response along the period of brine injection.

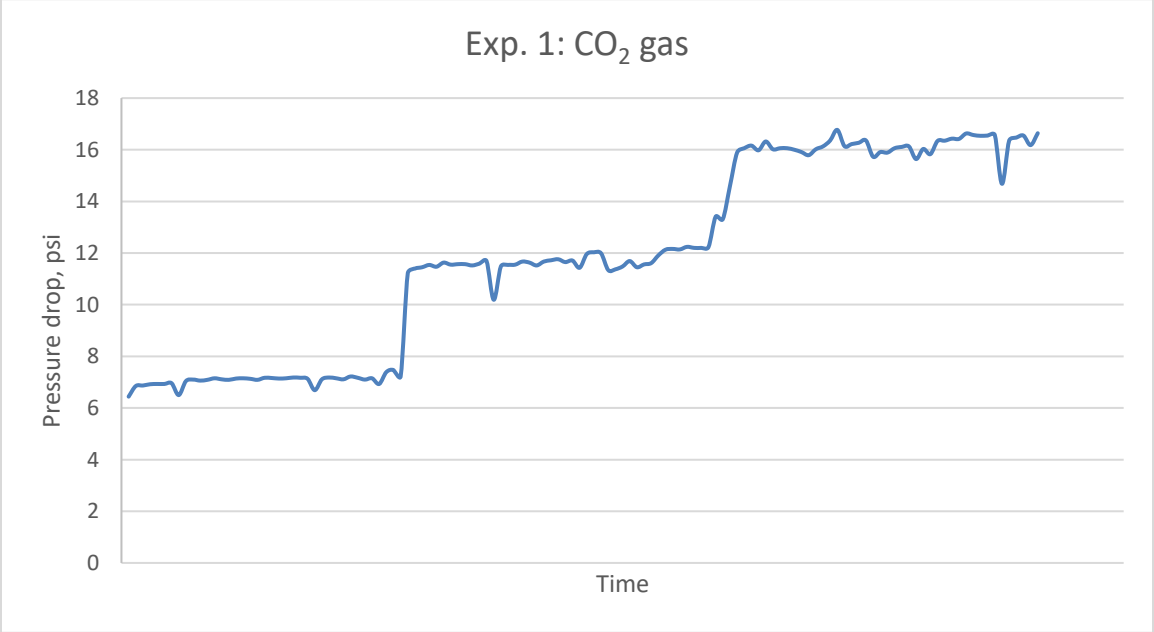

Figure 38: Pressure differential during formation brine injection in exp. 1

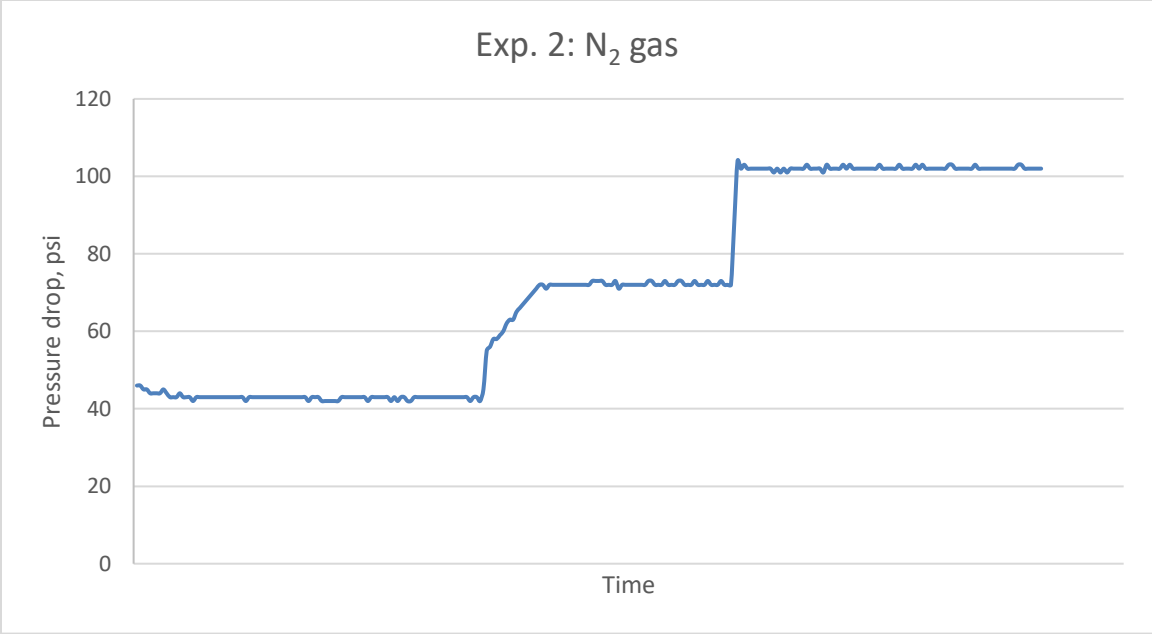

Figure 39: Pressure differential during formation brine injection in exp. 2

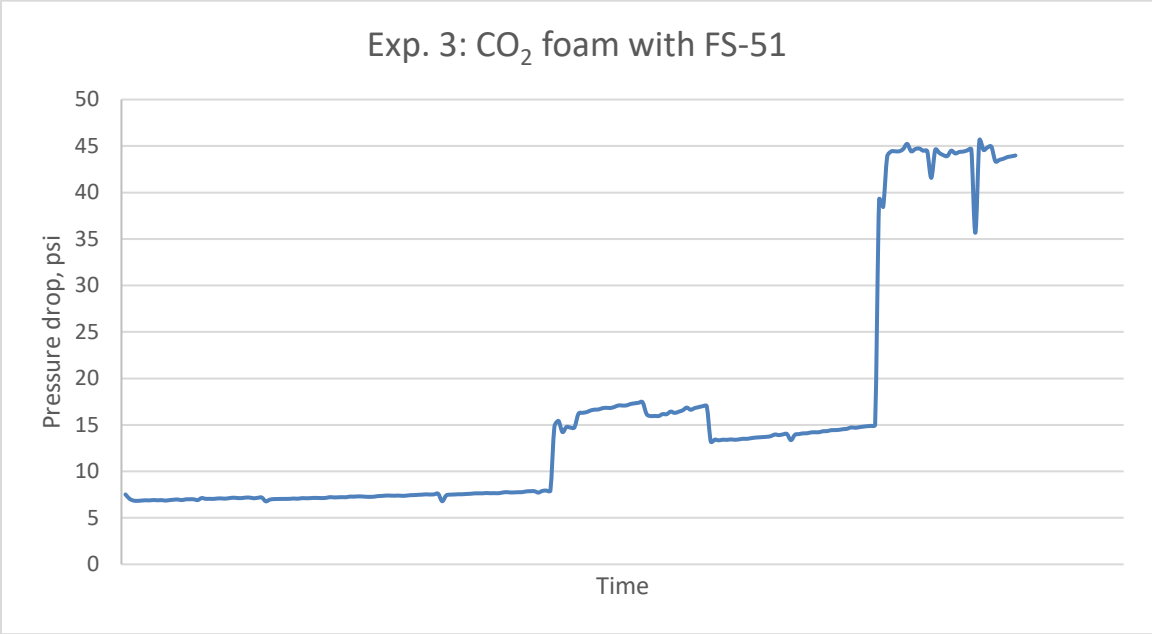

Figure 40: Pressure differential during formation brine injection in exp. 3

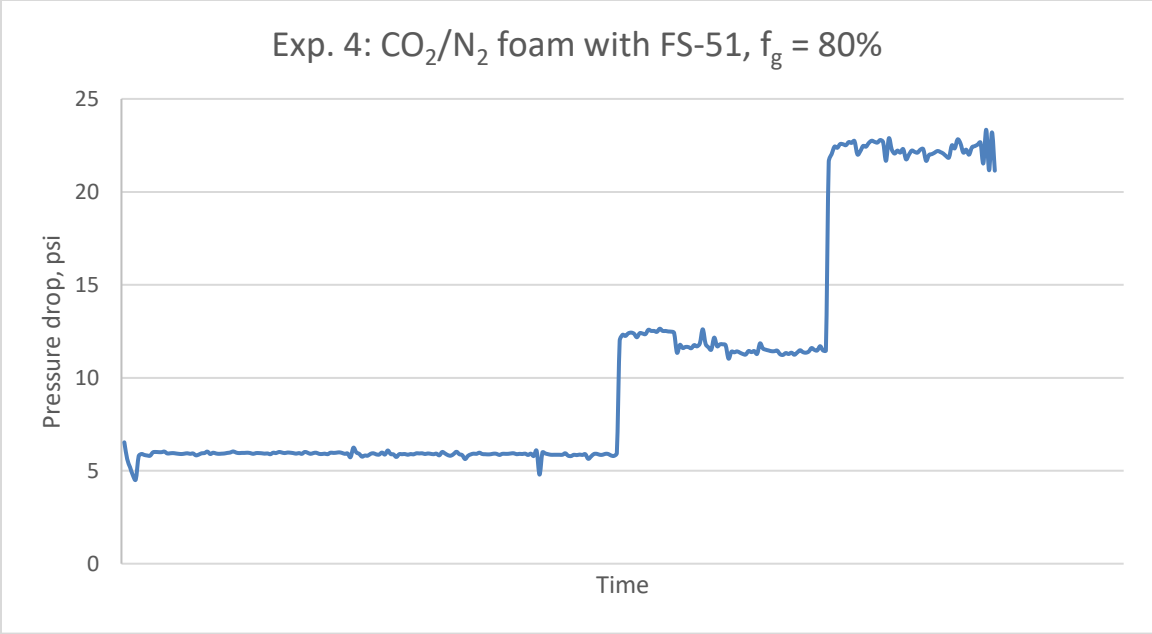

Figure 41: Pressure differential during formation brine injection in exp. 4

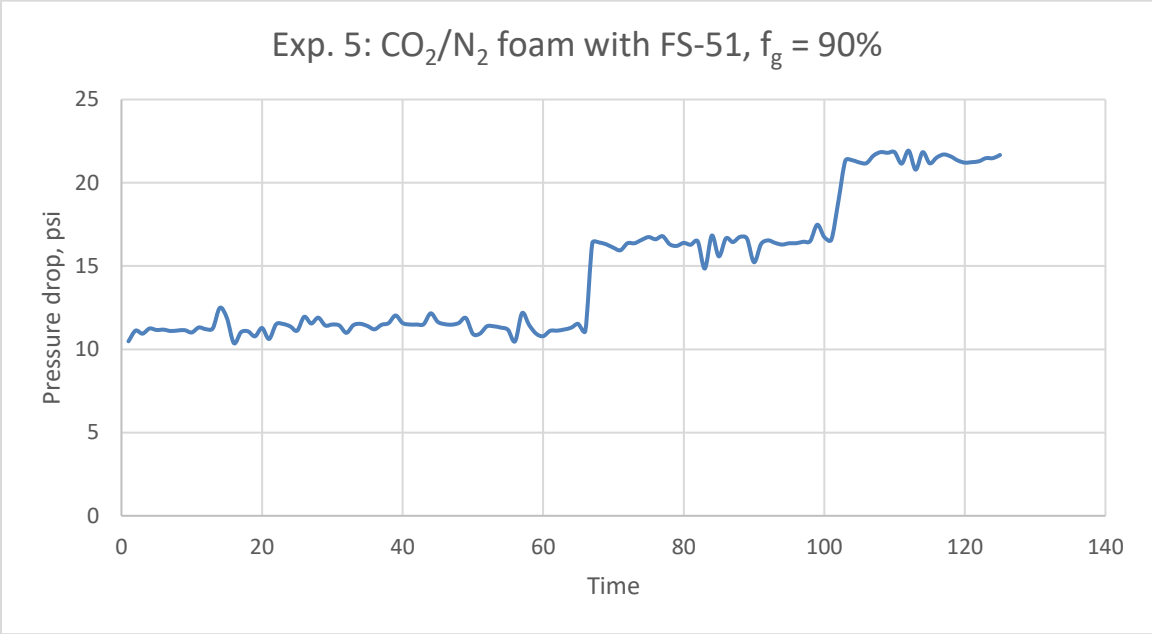

Figure 42: Pressure differential during formation brine injection in exp. 5

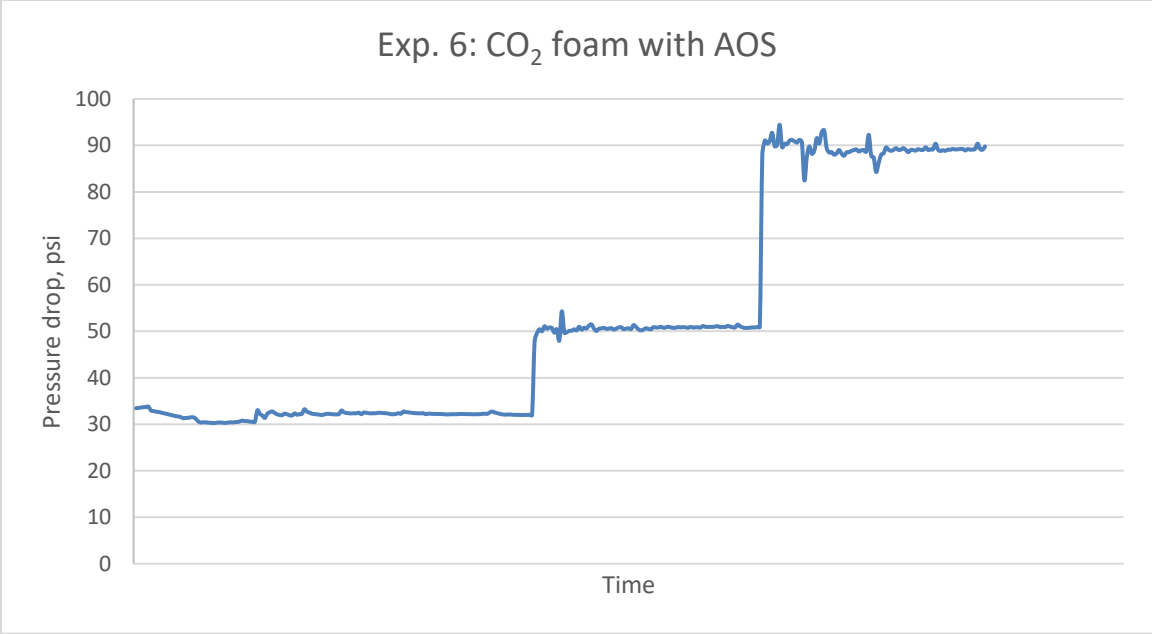

Figure 43: Pressure differential during formation brine injection in exp. 6

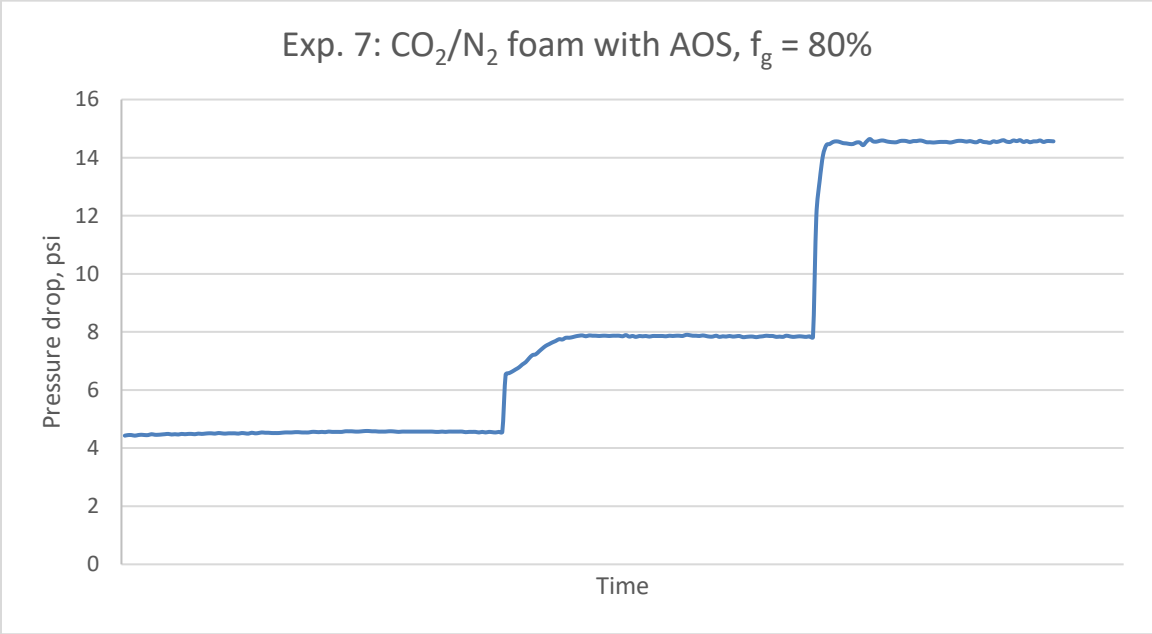

Figure 44: Pressure differential during formation brine injection in exp. 7

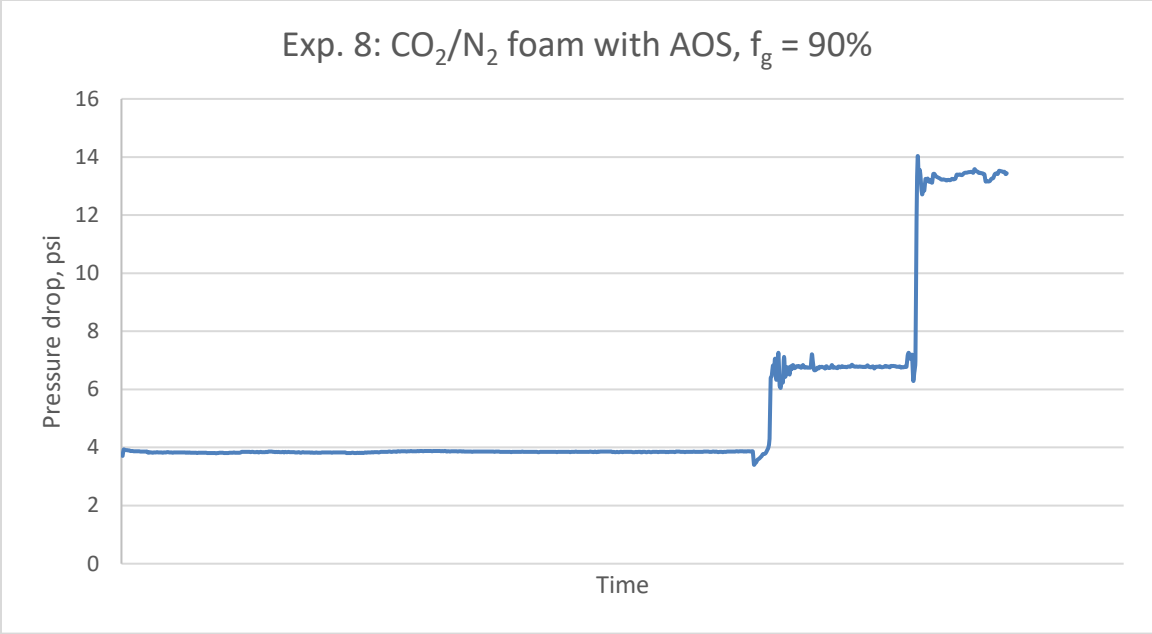

Figure 45: Pressure differential during formation brine injection in exp. 8

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